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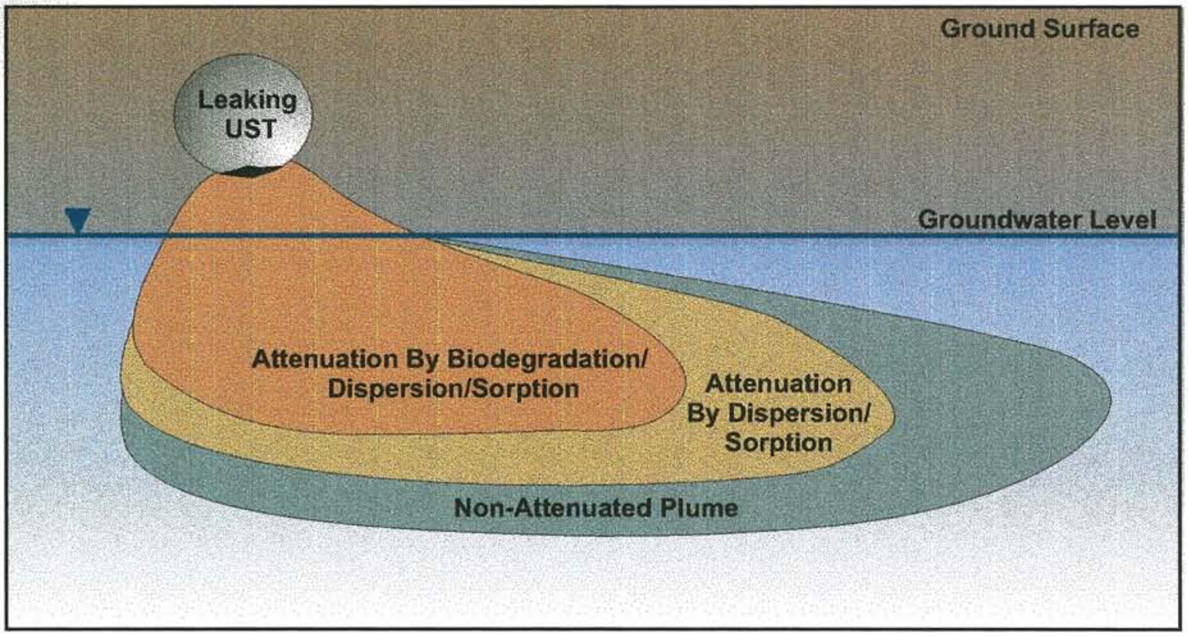
AFCEE
Natural Attenuation Initiative

Presentation of Technical Summary Reports



Air Force Center for Environmental Excellence

and

PARSONS ENGINEERING SCIENCE, INC.

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Report Documentation Page

Form Approved
OMB No. 0704-0188

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1. REPORT DATE	2. REPORT TYPE	3. DATES COVERED
11 JAN 2000	**Summary Results**	**00-00-2000 to 00-00-2000**

4. TITLE AND SUBTITLE **AFCEE Natural Attenuation Initiative Presentation of Summary Reports**	5a. CONTRACT NUMBER 5b. GRANT NUMBER 5c. PROGRAM ELEMENT NUMBER
6. AUTHOR(S)	5d. PROJECT NUMBER 5e. TASK NUMBER 5f. WORK UNIT NUMBER
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) **Parsons Engineering Science, Inc.,1700 Broadway,Suite 900,Denver,CO,80290**	8. PERFORMING ORGANIZATION REPORT NUMBER
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) **Air Force Center for Environmental Excellence, 3300 Sidney Brooks Rd., Brooks City Base, TX, 78235-5112**	10. SPONSOR/MONITOR'S ACRONYM(S) **AFCEE** 11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release; distribution unlimited

13. SUPPLEMENTARY NOTES

14. ABSTRACT
This document compiles the presentations given on January 11, 2000 for the Air Force Center for Environmental Excellence Natural Attenuation Initiative. In addition to opening and closing remarks this document contains the following technical summary reports: Natural Attenuation of Fuel Hydrocarbons -- Performance and Cost Results, Natural Attenuation of Chlorinated Solvents -- Performance and Cost Results, Stream-Lined Risk-Based Natural Attenuation Projects -- Performance and Cost Results, Light Nonaqueous-Phase Liquid Weathering at Various Release Sites -- Source Reduction Effectiveness Technical Summary.

15. SUBJECT TERMS
fuel hydrocarbons, natural attentuation, risk-based, LNAPL, source reduction, chlorinated solvents, MTBE, Methyl tertiary-Butyl Ether, weathering, DNAPL

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT **unclassified**	b. ABSTRACT **unclassified**	c. THIS PAGE **unclassified**	**Same as Report (SAR)**	**145**	

Standard Form 298 (Rev. 8-98)
Prescribed by ANSI Std Z39-18

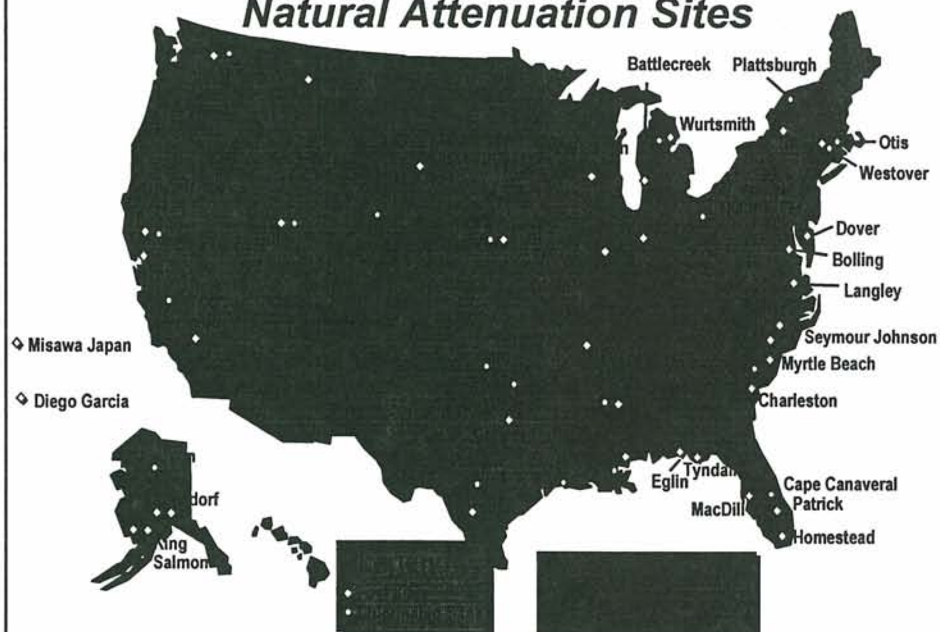
PRESENTATION AGENDA
AFCEE NATURAL ATTENUATION INITIATIVE
11 JANUARY 2000
BROOKS AFB, TEXAS

0830	Introductions and Overview of the AFCEE Natural Attenuation Initiative (Jerry Hansen and Todd Wiedemeier)
0845	Natural Attenuation of Fuel Hydrocarbons - Performance and Cost Results (Bruce Henry)
0930	Natural Attenuation of Chlorinated Solvents - Performance and Cost Results (Todd Wiedemeier)
1015	Break
1045	Stream-Lined Risk-Based Natural Attenuation Projects - Performance and Cost Results (John Hicks)
1130	Lunch Break
1230	Methyl tertiary-Butyl Ether – Its Movement and Fate in the Environment, and Potential for Natural Attenuation (Todd Wiedemeier)
1315	Light Nonaqueous-Phase Liquid Weathering at Various Release Sites (Bruce Henry)
1400	Break
1430	Source Reduction Effectiveness Technical Summary (John Hicks)
1515	Future Direction and Open Discussion
1545	Closing Remarks (Jerry Hansen and Todd Wiedemeier)
1600	Adjourn

Natural Attenuation Presentations

11 January 2000

AFCEE Tech Transfer Natural Attenuation Sites



Players

- AFCEE/ERT
- Parsons Engineering Science
- USEPA Kerr Lab
- Groundwater Services Inc
- COE Cone Penetrometer
- Utah State University
- USGS

Major Products

- Protocols: Fuels - 1995, Chlorinated - 1998
- Groundwater Models: Bioscreen, Bioplume III, Biochlor
- Small Sites Protocol
- Lessons learned reports: Fuels, Solvents, MTBE, LNAPL Weathering, Source Reduction
- Check AFCEE Web Site for info on obtaining copies

Agenda

- 0830 Introductions and Overview of the AFCEE Natural Attenuation Initiative (Jerry Hansen and Todd Wiedemeier)
- 0845 Natural Attenuation of Fuel Hydrocarbons - Performance and Cost Results (Bruce Henry)
- 0930 Natural Attenuation of Chlorinated Solvents - Performance and Cost Results (Todd Wiedemeier)
- 1015 Break
- 1045 Stream-Lined Risk-Based Natural Attenuation Projects - Performance and Cost Results (John Hicks)
- 1130 Lunch Break

Agenda (cont)

- 1230 Methyl tertiary-Butyl Ether – Its Movement and Fate in the Environment, and Potential for Natural Attenuation (Todd Wiedemeier)
- 1315 Light Nonaqueous-Phase Liquid Weathering at Various Release Sites (Bruce Henry)
- 1400 Break
- 1430 Source Reduction Effectiveness Technical Summary (John Hicks)
- 1515 Future Direction and Open Discussion
- 1545 Closing Remarks (Jerry Hansen and Todd Wiedemeier)
- 1600 Adjourn

Overview of the AFCEE Natural Attenuation Initiative

Presented by

Todd H. Wiedemeier

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AFCEE Natural Attenuation Initiative

- Work Began in 1993
- Joint Effort Between AFCEE, the USEPA, and Parsons ES
- Involved Evaluation of Natural Attenuation at Multiple Sites (70) in Various Geographic and all 10 EPA Regions

AFCEE Natural Attenuation Initiative

- Why Such a Large-Scale Effort
  - Contractors were Exploiting the Air Force (and still do)
  - AFCEE Wanted a "How To" Manual to Educate RPMs at Air Force Sites

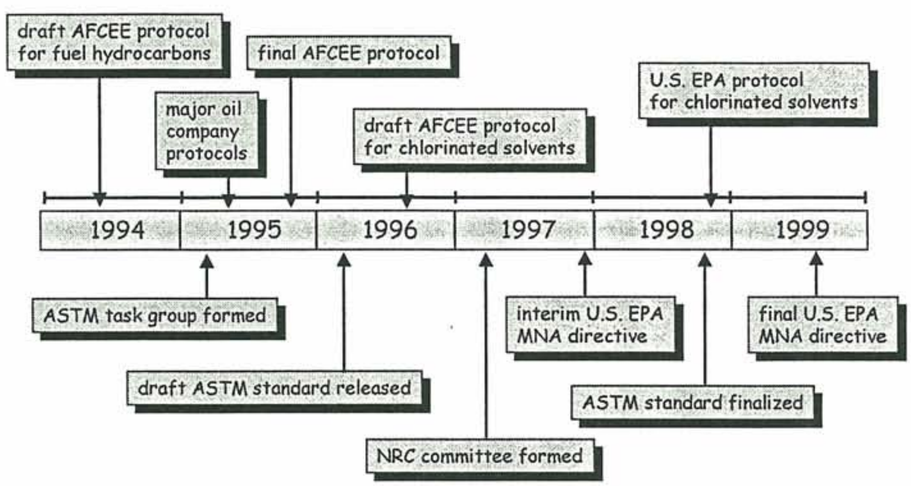
AFCEE Natural Attenuation Initiative

- AFCEE's Efforts led to a Greater Understanding of the Mechanisms of Natural Attenuation
- What AFCEE Learned is being used Across the Country and Around the World

Protocols Resulting from AFCEE's Efforts

- **Several Technical Guidance Documents have been Published as a Result of AFCEE's Efforts**
  - **1995 AFCEE Protocol for Evaluating Natural Attenuation of Fuels**
  - **1996 Draft AFCEE Protocol for Evaluating Natural Attenuation of Chlorinated Solvents**
  - **1998 EPA Technical Report for Evaluating Natural Attenuation Chlorinated Solvents in Groundwater (Modified From AFCEE 1996)**

Monitored Natural Attenuation Timeline



AFCEE Protocols

- The AFCEE Protocols Include the Most Comprehensive Description of Common Attenuation Mechanisms

- Both the Fuels and Solvent Protocols Include Detailed Methods for Quantifying Natural Attenuation

AFCEE Protocols

- Fuels Protocol Most Comprehensive Technical Guidance on the Subject

- Fuels Protocol has Been Accused of Being "Too Conservative" but no one has Ever Refuted the Strategy and Methodology of this Document – Right Type of Data

Weight of Evidence Approach

- All of the AFCEE Protocols (Including EPA, 1998) Rely on Independent and Converging Lines of Evidence to Document and Quantify Natural Attenuation

AFCEE Protocols

- Over 5,000 AFCEE Fuel Protocols Distributed Worldwide
- Over 4,000 AFCEE Chlorinated Solvent Natural Attenuation Protocols Distributed Worldwide (Does not include EPA Technical Report)

Conclusions

- **Much Progress has been made in Evaluating Natural Attenuation as a Remedial Approach**

- **Much of this Progress is the result of AFCEE's Efforts**

Natural Attenuation of Fuel Hydrocarbons Performance and Costs Results from Multiple Air Force Demonstration Sites

Presented by

Bruce Henry

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Natural Attenuation Initiative

- **Document the effectiveness and promote the use of monitored natural attenuation (MNA) to cost-effectively achieve cleanup and closure of fuel spill sites at Air Force facilities.**
- ***Technical Protocol for Implementing Intrinsic Remediation with Long-Term Monitoring for Natural Attenuation of Fuel Contamination Dissolved in Groundwater*** **(AFCEE Technical Protocol, 1995).**
- **Currently, at least 44 states and all 10 USEPA regions will consider the use of MNA as a viable remedy for fuel-contaminated groundwater.**

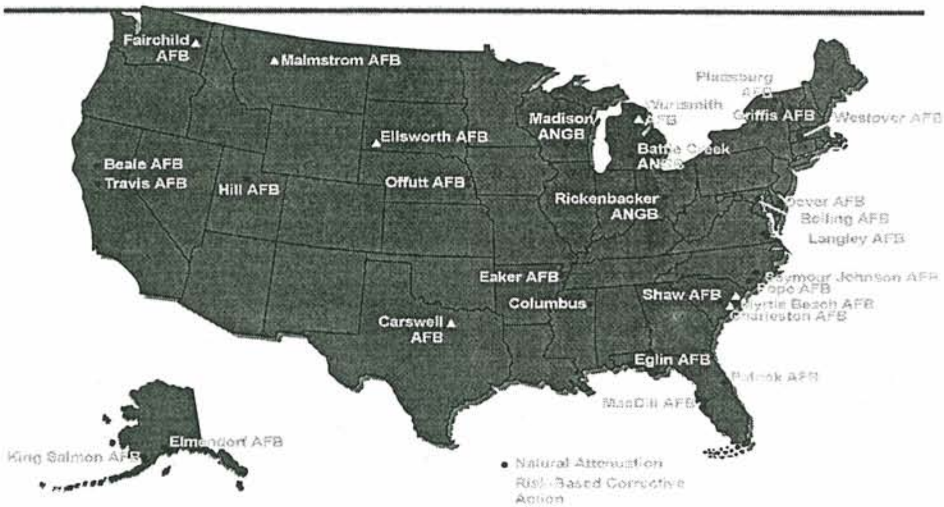
The United States Environmental Protection Agency (USEPA, 1999) Office of Solid Waste and Emergency Response (OSWER) defines MNA as:

...the reliance on natural attenuation processes (within the context of a carefully controlled and monitored clean-up approach) to achieve site-specific remediation objectives within a time frame that is reasonable compared to that offered by other more active methods. The "natural attenuation processes" that are at work in such a remediation approach include a variety of physical, chemical, or biological processes that, under favorable conditions, act without human intervention to reduce the mass, toxicity, mobility, volume, or concentration of contaminants in soil and groundwater. These in-situ processes include biodegradation; dispersion; dilution; sorption; volatilization; radioactive decay; and chemical or biological stabilization, transformation, or destruction of contaminants.

42 sites with a wide variety of environmental and contaminant conditions were investigated, including:

- **Site locations ranging from Alaska to Florida;**
- **Depths to groundwater ranging from 0 to 48 feet below ground surface (bgs);**
- **Plume areas ranging from 0.3 to 60 acres, and plume lengths of 100 to 3,000 feet;**
- **Average groundwater temperatures ranging from 5.5 to 26.9 degrees Celsius (^oC); and**
- **Soil types ranging from silty clay to coarse sand and gravel.**

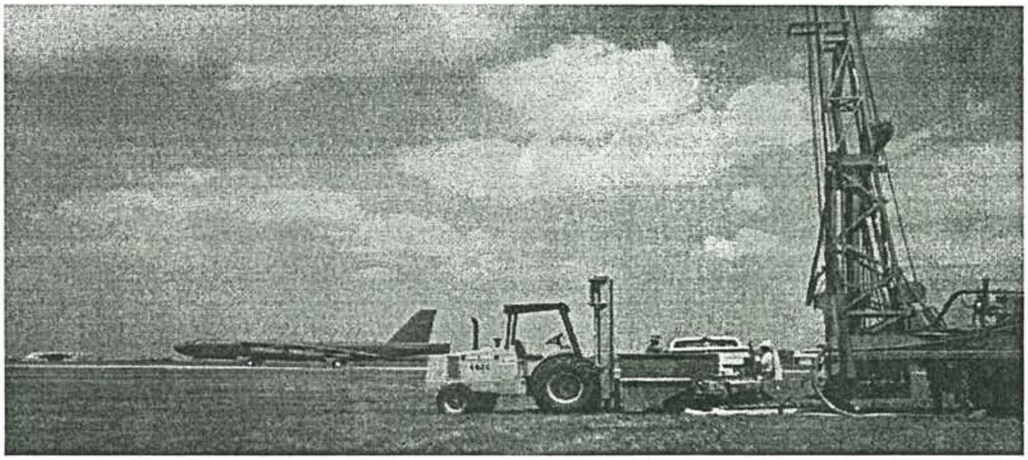
Natural Attenuation Initiative Locations



Treatability Study Objectives

- Develop efficient site characterization techniques to accurately document natural attenuation and to reduce overall expenditures of time and money.
- Identify those biological processes most responsible for contaminant attenuation.
- Determine rates of contaminant destruction.
- Use groundwater flow and solute fate and transport models to predict the effects of natural attenuation, both alone and in combination with engineered remedial technologies, on the future migration and persistence of dissolved BTEX.

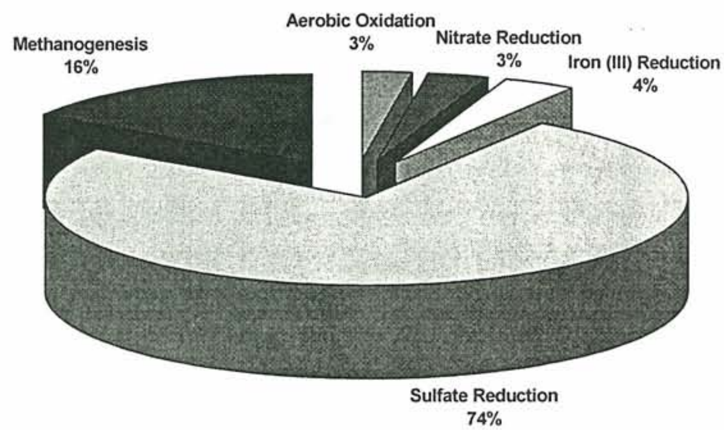
Drill Rig and Jet



Treatability Study Results

- Dissolved BTEX compounds are undergoing natural attenuation (biodegradation) at all 42 Air Force test sites representing a broad range of environmental conditions.
- The majority of dissolved BTEX plumes were either stable or receding (historical data or model predictions).
- The average relative contribution of each primary biodegradation process to the total assimilative capacity of the groundwater system decreased in the following order: sulfate reduction, methanogenesis, iron reduction, denitrification, and aerobic oxidation.

Average Relative Contribution of BTEX Biodegradation Processes in Site GW



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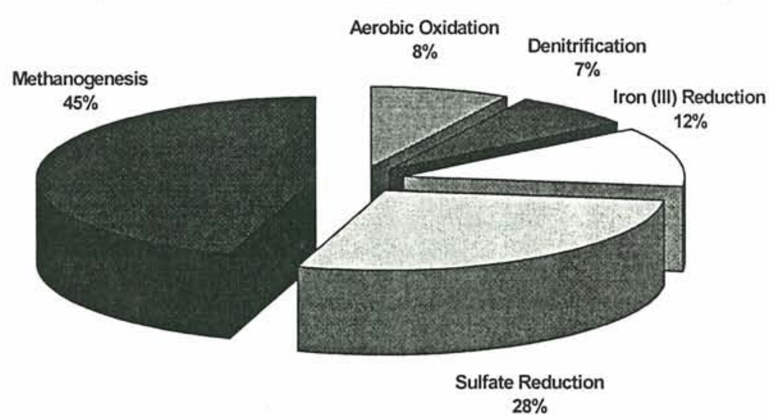
Average Relative Contributions of BTEX Biodegradation Processes in Site GW

(Excluding 5 Sites with >200mg/l Sulfate Reduction Capacity)



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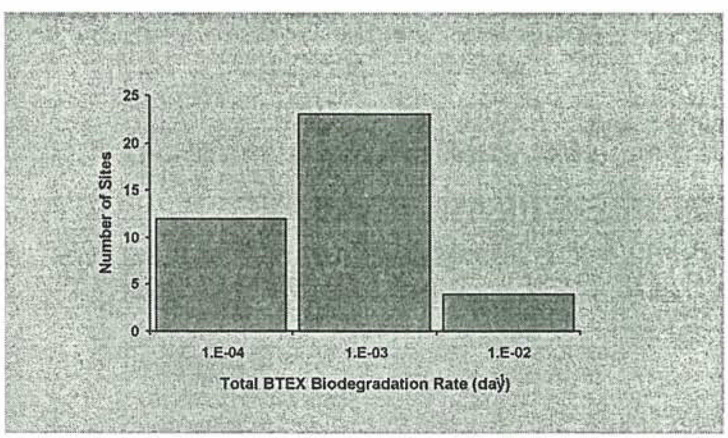
Treatability Study Results (continued)

- The total BTEX assimilative capacity of groundwater averaged 64 milligrams per liter.
- The field-scale biodegradation rate constants ranged from 0.0002 to 0.08 percent per day (day^{-1}), with a geometric mean value of 0.0019 day^{-1}. Or, biodegradation half-lives of 9.5 years to 9 days, with a mean half-life of 1 year.

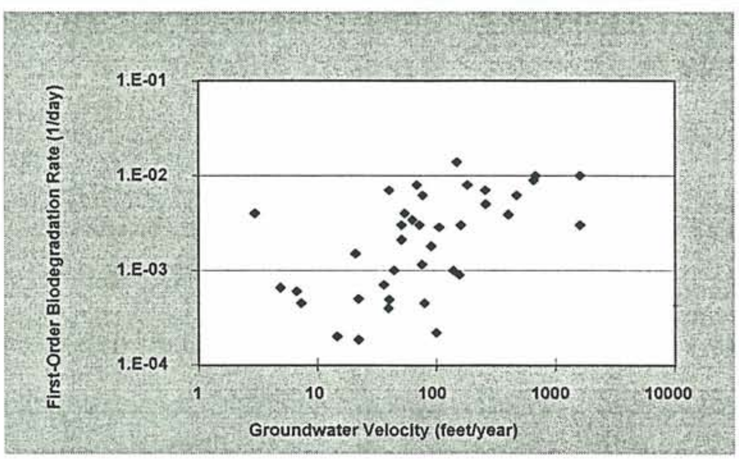
Estimated BTEX Biodegradation Rates



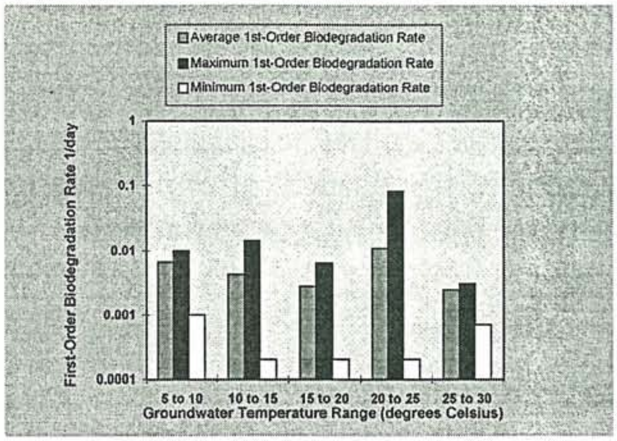
Treatability Study Results (continued)

- There was some correlation between field biodegradation rates and groundwater velocity; correlation between biodegradation rates and groundwater temperature, assimilative capacity, and plume length were not apparent.

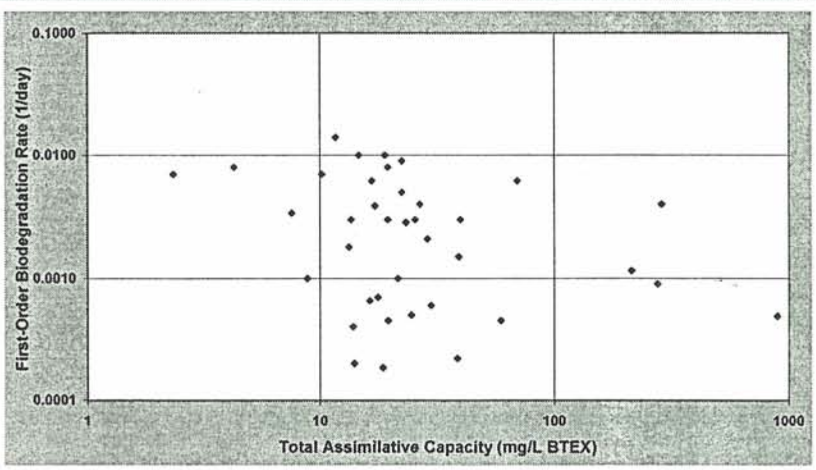
Biodegradation Rate versus Groundwater Velocity



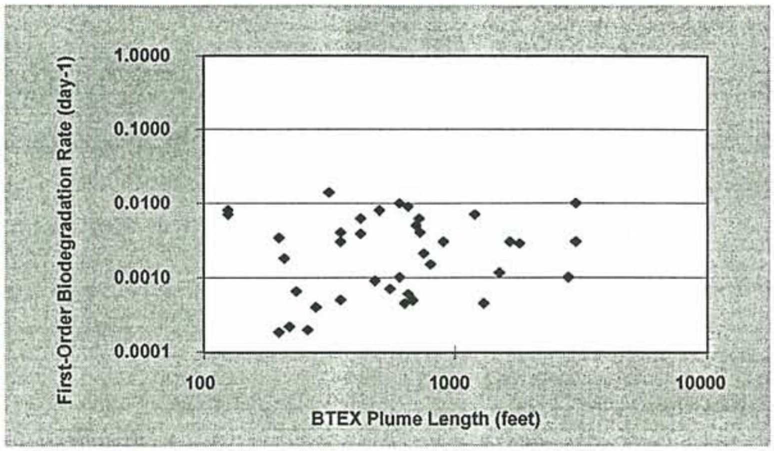
First-Order Biodegradation Rate versus Groundwater Temperature



Biodegradation Rate versus Total Assimilative Capacity



First-Order Biodegradation Rate versus BTEX Plume Length



Are these correlations, or lack thereof, significant?

- **Biodegradation of BTEX compounds was documented under ALL environmental conditions encountered.**
- **Biodegradation, in conjunction with the non-destructive mechanisms of natural attenuation (advection, dispersion, and sorption), was significant enough to stabilize or attenuate groundwater plumes at the majority of sites.**

Treatability Study Results (continued)

- The average predicted time frame for dissolved BTEX to naturally attenuate below regulatory cleanup standards is conservatively estimated at 30 years. Engineered source reduction typically is required to attain cleanup standards in less than 20 years.

Treatability Study Results (continued)

- The average cost per site for completing Geoprobe® site characterization, laboratory analysis, data analysis, fate and transport modeling, and reporting was $126,000. Slightly higher costs (up to $136,000) were incurred at sites where conventional auger drilling was required due to groundwater depth.

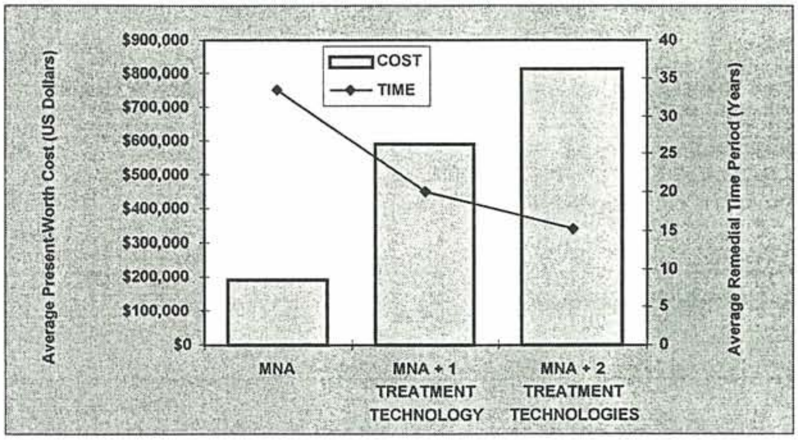
Typical Natural Attenuation Treatability Study Costs

Task	Hollow-Stem Auger	CPT	Geoprobe®
Site Visit/Technical Support	$ 9,960	$ 9,690	$ 9,690
Work Plan/Regulatory Approval	$19,300	$19,300	$19,300
Field Work Labor	$13,900	$13,900	$13,900
Field Work ODCs			
• Survey/Supplies/Per Diem	$ 9,150	$ 9,150	$ 9,150
• Drilling	$12,800	$11,500	$ 2,300
• Data Analysis/Analytical	$15,300	$15,300	$15,300
Modeling	$15,000	$15,000	$15,000
Treatability Study Report	$40,500	$40,500	$40,500
Total Project:	**$136,000**	**$134,000**	**$126,000**

Treatability Study Results (concluded)

- **Recommended LTM programs for MNA included an average network of 11 wells with a duration of 22 years, and had an average total program cost of $192,000.**
- **At many sites, natural attenuation processes had stabilized the groundwater plume, but engineered source remediation was recommended to reduce the duration and cost of LTM.**

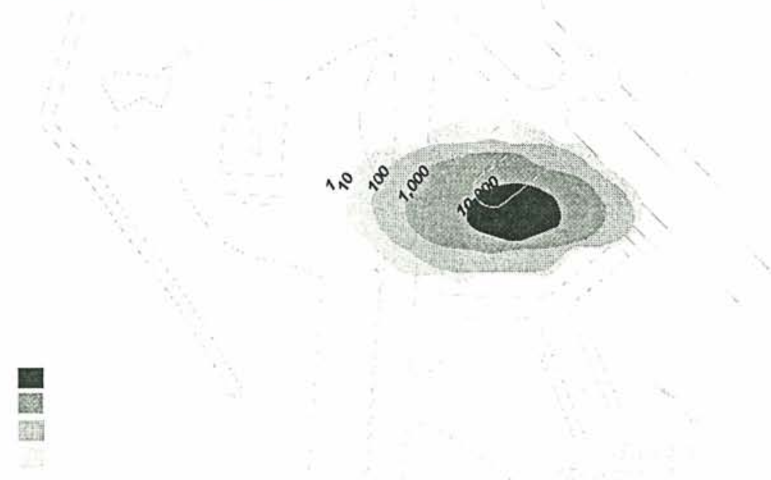
Time and Cost Relationship for Remedial Alternatives



Case Study: MacDill AFB Service Station Site 56

Service Station Fuel Release Site

Calibrated Total BTEX Plume



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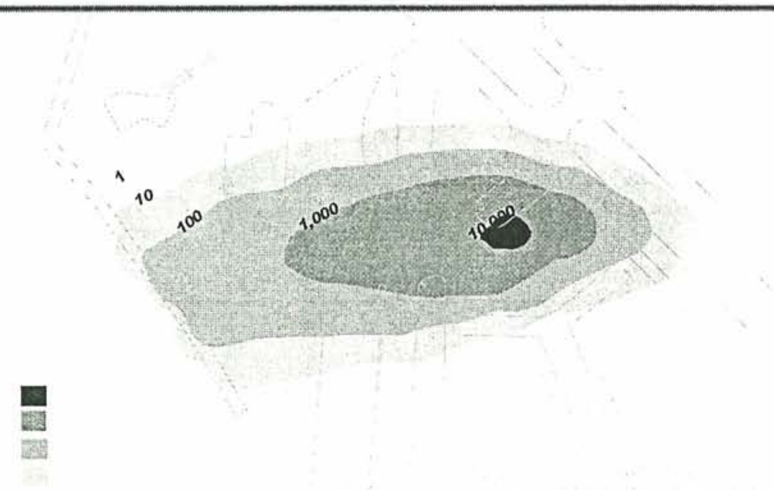
Simulated Total BTEX at 10 Years



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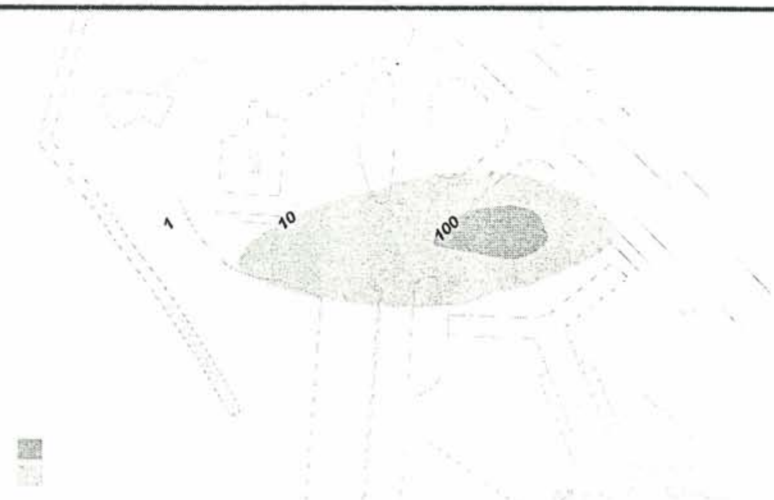
Simulated Total BTEX at 50 Years



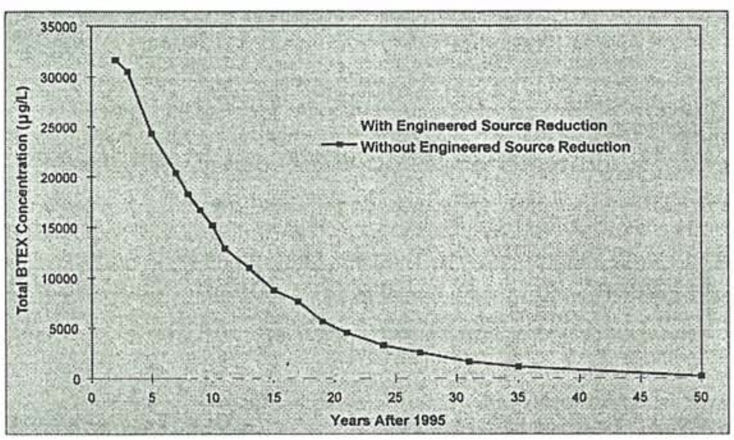
Site 56 Remedial Alternatives

- 1. RNA with LTM and Institutional Controls
  - BTEX in GW > RAO for 50 years
  - BTEX in SW may exceed RAO
  - Present worth cost $250,000
- 2. RNA/LTM + Bioventing/SVE
  - BTEX in GW > RAO for 10 years
  - BTEX at ditch reduced by 1/2
  - Present worth cost $348,000

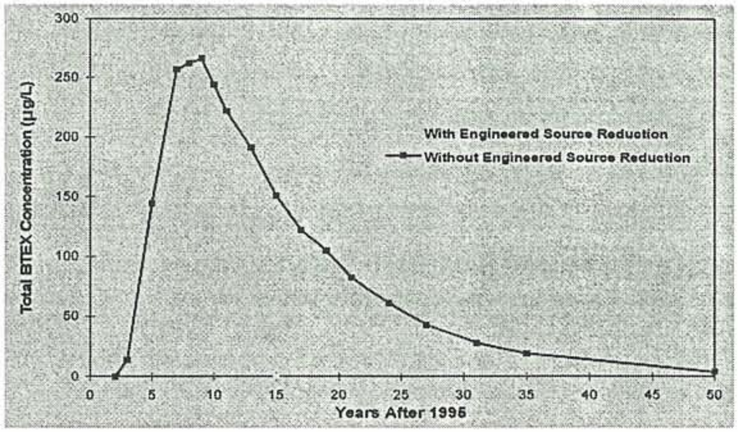
Site 56 Remedial Alternatives (continued)

3. Same as Alt. 2 + Limited GW Extraction
   - BTEX in GW > RAO for 6 years
   - Present worth cost $486,000
4. RNA/LTM + Soil Excavation
   - Same effects as Alternative 2
   - Suitable if station closes
   - Present worth cost $333,000

Comparison of Simulated BTEX Concentrations at Source Area



Comparison of Simulated BTEX Concentrations at Drainage Ditch



Summary of Remedial Alternatives

Remedial Alternative	Time Frame to Remediation	Present Worth Cost Estimate
Alternative 1		
- Intrinsic Remediation - Long-Term Monitoring - Institutional Controls	Long-Term Monitoring - 50 years	$250,000
Alternative 2		
- Bioventing/Biosparging - Soil Vapor Extraction (SVE) - Intrinsic Remediation - Long-Term Monitoring - Institutional Controls	Active Remediation - 3 years. Long-Term Monitoring - 14 years	$348,000
Alternative 3		$486,000
- Groundwater Extraction - Bioventing/Biosparging - Intrinsic Remediation - Long-Term Monitoring	Active Remediation - 3 years Long-Term Monitoring - 10 years	
Alternative 4		$333,000
- Soil Excavation - Intrinsic Remediation - Long-Term Monitoring	Active Remediation - 3 months Long-Term Monitoring - 14 years	

Site 56 Recommendations

- Alternative 2 achieves best combination of risk reduction and cost effectiveness
- If station closes, Alternative 4 may be most appropriate

Lessons Learned:

- Natural attenuation with biodegradation of fuel hydrocarbons is ubiquitous throughout the environment.
- Natural attenuation rates were rapid enough to stabilize hydrocarbon plume migration even when groundwater velocities were relatively high.
- Evaluate natural attenuation as a preferred remedy for fuel-contaminated groundwater before considering other more costly alternatives.

Lessons Learned (continued):

- **In cases where engineered remediation is required to lessen the remediation time frame or to protect potential receptors, low-cost, *in situ* source reduction (e.g., bioventing, SVE, and biosparging) should be considered to speed the remediation process.**
- **More costly remediation techniques (e.g., groundwater extraction and treatment) should be implemented only if the plume poses an imminent threat to human health or the environment.**

Lessons Learned (continued):

- **Important factors to consider when using MNA are the required level of groundwater modeling and the potential value of source reduction technologies in reducing LTM time frames and obtaining regulatory acceptance of a site closure strategy.**

Lessons Learned (concluded):

- **AFCEE/ERT and Parsons ES have implemented a streamlined risk-based site closure program that incorporates the "lessons learned" from natural attenuation studies.**
- **Under this program, fuel-contaminated sites are obtaining MNA site closure agreements at half the cost of the original natural attenuation TSs.**

Special Considerations:

- **With the majority of fuel hydrocarbon plumes either stable or receding, the focus of site remediation shifts to the <u>persistence</u> of contaminants in groundwater at levels above regulatory guidelines.**
- **Several states have published guidance or regulations regarding the conduct of natural attenuation studies.**
- **Some regulatory agencies may have restrictions on the time frame for remediation by natural attenuation (e.g., State of Florida - 5 years)**

Special Considerations (concluded):

- Property transfer or sale may impose time constraints on remediation (base closures, real estate sales).
- Responsible parties are subject to continuing environmental liability during the long-term remediation.
- No guarantees that regulatory guidelines will not change in the future (e.g., time frame to remediate, possible enforceable guidelines for MTBE).

Natural Attenuation of Chlorinated Solvents - Performance and Cost Results from Multiple Air Force Demonstration Sites

Presented by

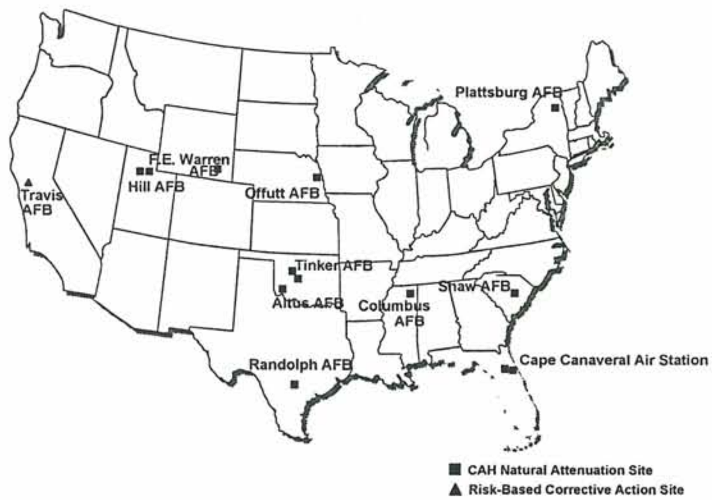
Todd H. Wiedemeier

PARSONS
PARSONS ENGINEERING SCIENCE, INC.

AFCEE Natural Attenuation Initiative – Chlorinated Solvents

- **Began in 1995**
- **Total of 13 Sites were Evaluated Across the Country**
- **Additional Sites were Evaluated under the Risk-Based Corrective Action Program (Travis AFB) and Other Programs (Williams AFB and MMR)**

Air Force Natural Attenuation Initiative for Chlorinated Solvents



Project Elements

- Site Visit/Kickoff Meeting
- Site-Specific Work Plan
- Field Site Characterization (Geoprobe® or CPT rig)
- Data Interpretation
- Contaminant Fate and Transport Modeling
- Treatability Study Report
- Final Regulatory Meeting

Groundwater Analytical Protocol Developed by AFCEE

- Contaminants/ Daughter Products
- Dissolved Oxygen
- Nitrate/Nitrite
- Fe(II)
- Sulfate/Sulfide
- Methane
- Oxidation/Reduction Potential (ORP)
- Carbon Dioxide
- Alkalinity
- pH
- Temperature
- Total Organic Carbon[a/]
- Ethene/Ethane[a/]
- Chloride[a/]
- Hydrogen[a/]

a/ Chlorinated Solvents Only

Wide Range of Site Characteristics

- Depths to groundwater ranging from 0 to 60 feet bgs
- Plume areas ranging from 1.6 to 210 acres
- Average groundwater temperatures ranging from 9.1 to 25.6 °C
- Aquifer matrices ranging from clay to coarse sand and gravel
- TCE most pervasive, followed by cis-1,2-DCE

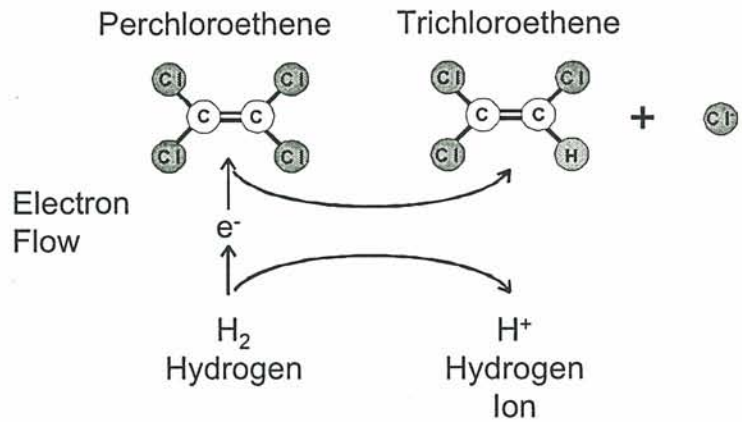
What Did We Learn from all This Variability?

- Solvent Plumes are Like Children, Each one is Different
- Plume Behavior (i.e., stable, shrinking, growing) Depends on Prevailing Groundwater Geochemistry
- Why?

Because ....

- The Common Chlorinated Solvents, PCE, TCE, Carbon Tetrachloride, and 1,1,1-TCA Predominantly Biodegrade in the Natural Environment via a process Called Reductive Dechlorination

Reductive Dechlorination



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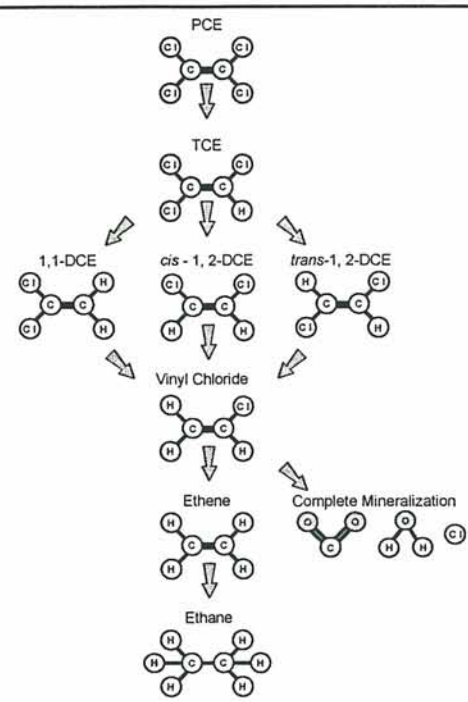


Anaerobic Reductive Dehalogenation

Requirements for Reductive Dechlorination

- Reductive Dechlorination only Occurs Under very Strongly Reducing (Anaerobic) Conditions (e.g. Sulfate Reducing or Methanogenic)
- What is required for Strongly Reducing Conditions?
  - A Source of Oxidizable Organic Carbon

Effect of Prevailing Groundwater Geochemistry

- The Presence and Amount and Type of Oxidizable Organic Carbon Determines how a Solvent Plume Behaves in Groundwater
- Based on AFCEE's Experience at Multiple Air Force Bases, it was determined that Plume Behavior Could be Grouped into Three Categories

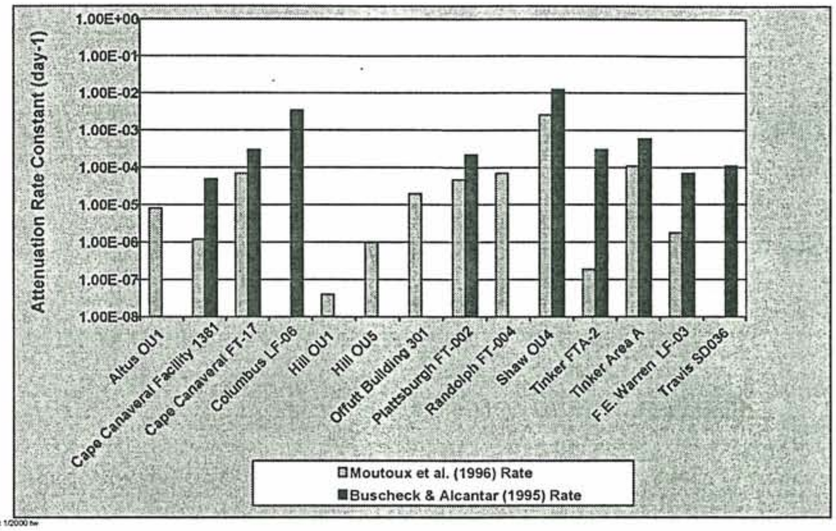
Wide Range of Plume Behavior

- Type 1 - anthropogenic carbon drives reductive dechlorination
- Type 2 - native organic carbon drives reductive dechlorination
- Type 3 - low carbon levels, little or no reductive dechlorination
  - Nine sites had a mixture of Type 1 plus Type 2 or 3; two sites with mixture of Type 2 and 3, three sites with primarily Type 1

Calculation of Field Biodegradation Rates

- Use of a biologically conservative tracer
- Method of Buscheck & Alcantar (1995) for steady-state plumes
- Method of Moutoux *et al.* (1996)

Estimated Attenuation Rates for Total Chlorinated Ethenes



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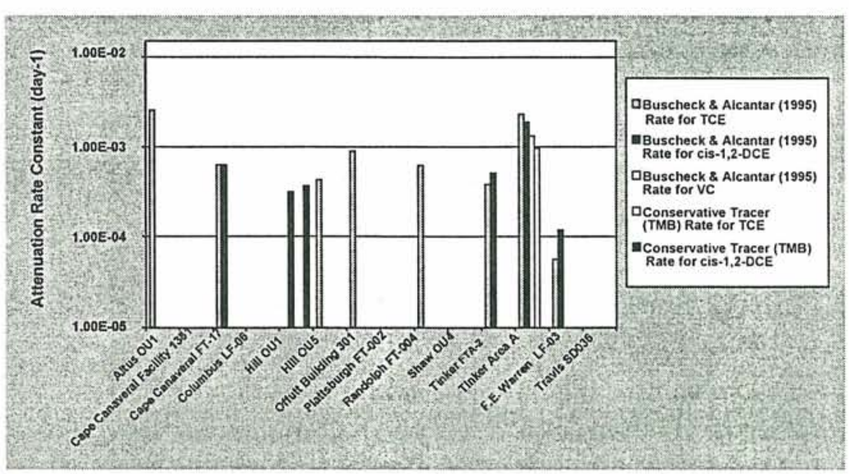
Estimated Attenuation Rates for TCE, DCE, and VC



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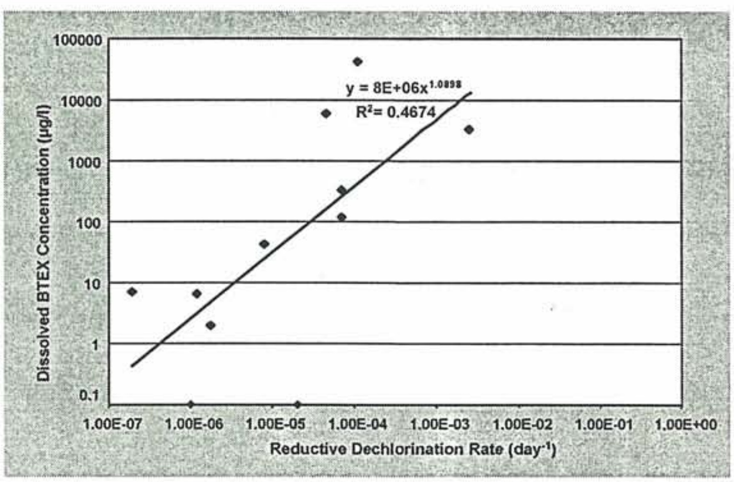
Summary of Total Destructive Attenuation Rates

Compounds	No. of Rates	Geometric Mean (day^{-1})	Half-Life (yr)	Median (day^{-1})	Half-Life (yr)
Total Chlorinated Ethenes	8 (B&A)	4.0×10^{-4}	4.7	2.6×10^{-4}	7.3
Trichloroethene	5 (B&A) 1 (TMB)	5.2×10^{-4} 7.0×10^{-4}	3.7 2.7	5.0×10^{-4}	3.8 (0.4)*
cis-1, 2-Dichloroethene	4 (B&A) 1 (TMB)	3.7×10^{-4} 3.0×10^{-4}	5.1 6.3	3.8×10^{-4} —	5.0 (0.5)* —
Vinyl Chloride	1 (B&A)	1.0×10^{-4}	1.9	1.0×10^{-4}	1.9 (0.4)*

Maximum BTEX Concentration vs. Biodegradation Rate



Solute Fate and Transport Modeling

- Numerical Models were used to Predict the Fate and Transport of Solvents in Groundwater
- Modflow/MT3D

Solute Fate and Transport Modeling

- Out of 13 Plumes Models Predicted:
  - 2 Plumes at Steady-State
  - 1 Plume Expanding Along Sewer Line Corridors
  - 4 Plumes Discharging to a Surface Water Body
  - 6 Plumes Expanding (250 to 9,500 ft)

Predicted CAH Plume Persistence

- Estimated time required for natural attenuation alone to achieve cleanup goals:
  - 17 to >200 years
  - >100 years for 6 of 12 sites

Predicted CAH Plume Persistence

- If engineered source reduction and/or hotspot pumping performed, predicted cleanup times exceeded lengths of simulation periods (35-200 years) at 6 of 11 sites; timeframe decreased 0 to 90% (avg 44%) at remaining 5 sites

Conclusions from Modeling Effort

- In Many Cases, Groundwater Quality Standards may not be Achieved within 100 years Without Aggressive Remedial Actions in the Source Area

Conclusions from Modeling Effort

- In Some Cases, Soil Remediation has Minimal Impact on the Total Time Frame Required for Natural Attenuation to Achieve Cleanup Goals for Groundwater

Modeling Limitations

- Available Models used First-Order Decay Rates
- Source Characteristics, History, and Weathering Rate Often Unknown--Simulated as "Black Box"

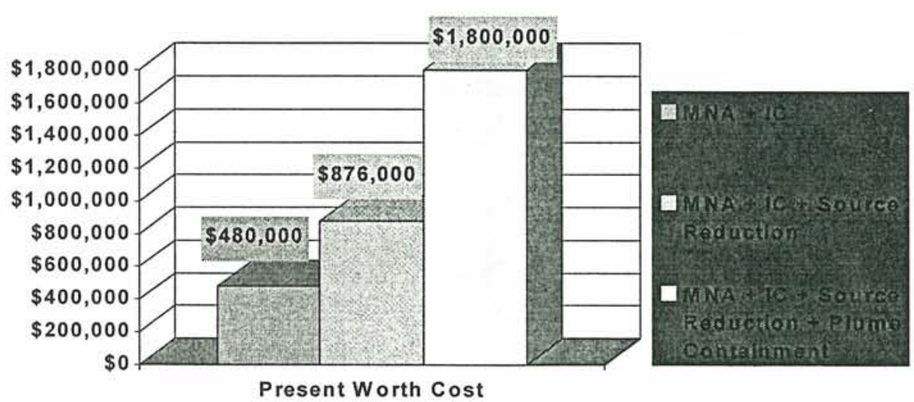
Modeling Limitations

- Fate and Transport of Parent and Daughter Compounds Could not be Simulated Simultaneously
- Earlier Model Versions did not Allow Spatial Variability of Input Parameters

Proposed Remedial Alternatives

- MNA +IC: 2 sites (out of 14)
- MNA, IC, + engineered source reduction and/or hotspot pumping: 7 sites
- MNA, IC, + downgradient plume cutoff: 4 sites
- Insufficient data for recommendation: 1 site

Remedial Alternative Cost Comparisons



Long-Term Monitoring

- Recommended number of LTM wells ranged from 8 to 30 and averaged 17
- LTM of surface water recommended at 9 sites
- Recommended sampling frequencies ranged from 1 to 2 years (annual sampling most frequently recommended)

Typical Natural Attenuation Treatability Study Costs

Task	Geoprobe®/Cone Penetrometer
Site Visit/Technical Support[a/]	$9,010
Work Plan/Regulatory Approval[b/]	$20,300
Field Work Labor	$9,760
Field Work Other Direct Costs (ODCs)	
Survey/Supplies/Per Diem	$6,150
Geoprobe®/Cone Penetrometer Operation	$878
Data Analysis/Analytical	$18,200
Total Field Work ODCs	$25,300
Modeling	$19,400
Treatability Study Report[c/]	$38,100
Total Project	$122,000

a/ Includes kickoff meeting, post-reporting meeting, and regulatory support.
b/ Includes draft and final versions, and gathering/analyzing available site data.
c/ Includes draft and final versions, with formal written responses to review comments on the draft report.

Findings of Natural Attenuation Evaluations - Solvents

- Intrinsic Bioremediation Occurring at Approximately 88% of the Sites Studied (Biased, Probably 40%)
- Reductive Dechlorination Occurring at 100% of Sites Impacted with Fuels
- Surface Water Impacted at Many Sites
- 6 of 13 Plumes Expected to Grow

What Does all of This Mean?

- Some Form of Engineered Remediation may be Required at Many Sites
- Is Pump and Treat the Answer?
- ABSOLUTELY NOT!!!
- Why?

Engineered Bioremediation of Chlorinated Solvents

- **Because Pump and Treat is Expensive and Doesn't Work**
- **The Limiting Factor at Many Sites Contaminated with Chlorinated Solvents is the Lack of Suitable Oxidizable Organic Carbon**

Engineered Bioremediation of Chlorinated Solvents

- **Many Types of Organic Substrate Have Been Added to Groundwater to Stimulate Biodegradation of Solvents Including:**
  - **Propionate**
  - **Lactate**
  - **Butyrate**
  - **Molasses**
  - **Hydrogen Releasing Compound®**
  - **Hydrogen ("Hindenberg Experiment")**

Engineered Bioremediation of Chlorinated Solvents

- All of These Materials are Added to Stimulate the Production of Hydrogen for Reductive Dechlorination
- All are Soluble to Some Extent in Water and Many are Miscible
- This Means Continuous Injection or at a Minimum, Multiple Injections (With the Exception of HRC®)

VegOil for Engineered Bioremediation of Chlorinated Solvents

- Injection of Food-Grade Vegetable Oil as a Carbon Substrate Looks Promising
- VegOil is a Non Aqueous Phase Which Means one Time Injection and Slow Dissolution

Conclusions and Recommendations

- The Air Force Should Require Evaluation of Natural Attenuation Before Considering Other Alternatives
- State-of-the-art Modeling Software and "Realistically Conservative" Assumptions Should be Used to Obtain More Plausible Results and Facilitate Evaluation of Remedial Alternatives

Conclusions and Recommendations

- Pounds of Contaminants Removed via Natural Attenuation Alone Should be Compared Against other Remedial Alternatives – People Will be Amazed
- If Engineered Remediation is Required the Focus Should be on In Situ Source Reduction Techniques

Recommendations (continued)

- More Costly Remediation Techniques Should be Considered only if the Plume Poses a Threat to Human Health or the Environment
- Hot-Spot Pumping or Air Sparging may Result in Aerobic Groundwater Conditions – Could Ruin the Natural Treatment System

Streamlined and Cost-Effective Closure of Petroleum Contaminated Sites

Presented by

John R. Hicks

PARSONS

PARSONS ENGINEERING SCIENCE, INC.

Objectives

- Demonstrate a more affordable risk-based site closure process for small petroleum sites
- Take advantage of RBCA rules recently promulgated by many states, and of increasing acceptance of natural attenuation as a remedial alternative

Site Descriptions

- 9 sites in 4 states (TX, MS, FL, NC)
- 6 gas stations, 1 fire training area, 1 jet fuel pipeline leak, 1 heating oil tank farm
- Size of contaminated area ranges from 1 to 7 acres (average 2.5 acres)

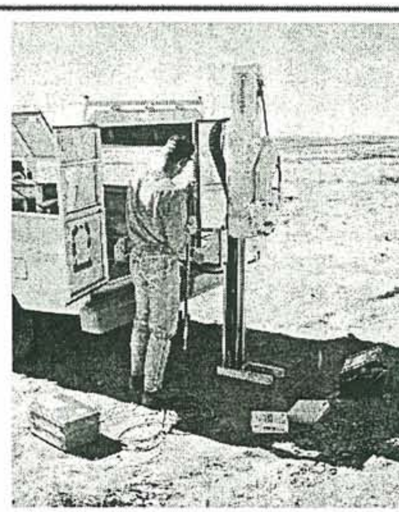
Air Force Streamlined Risk-Based Closure Initiative Locations

Project Elements

- Field site characterization
- Tier 1 screening to determine COPCs
- Natural attenuation analysis
- BIOSCREEN fate and transport modeling
- Tier 2 risk assessment
- Optional focused feasibility study

Typical Scope of Field Activities

- Use a Geoprobe® to collect soil samples and install small-diameter groundwater monitoring points (inexpensive, easy to use, no wastes)
- Average 4 days of field work

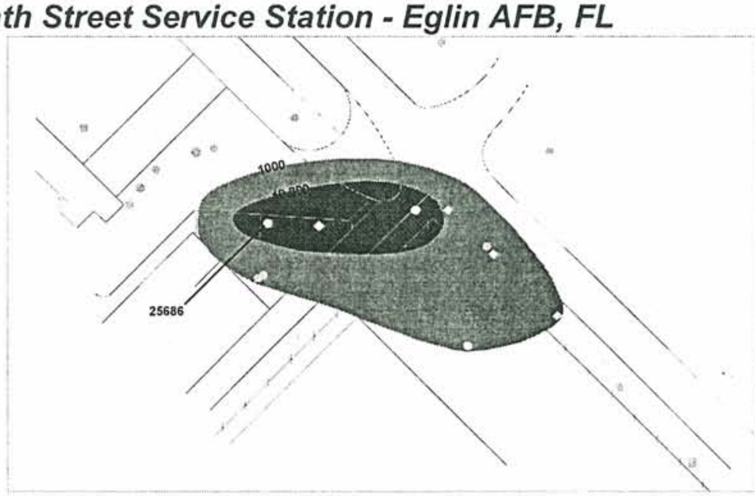


Case Study: Seventh Street Service Station, Eglin AFB, FL

- **Gasoline leak reported 1983 (est. 3600 gal)**
- **2 product recovery wells, 6 GW recovery wells, air stripper, operational 1989**
- **Recirculating bioventing system installed 1992**
- **Periodic groundwater monitoring**

BTEX in Groundwater

Seventh Street Service Station - Eglin AFB, FL



Tier 1 Screening

- Identify chemicals of potential concern
- Conservative, generic RBSLs typically available in look-up tables prepared by the State
- Sometimes developed for industrial sites
- No soil gas RBSLs developed--used OSHA PELs/TLVs

Tier 1 Screening Summary

Seventh Street Service Station - Eglin AFB, FL

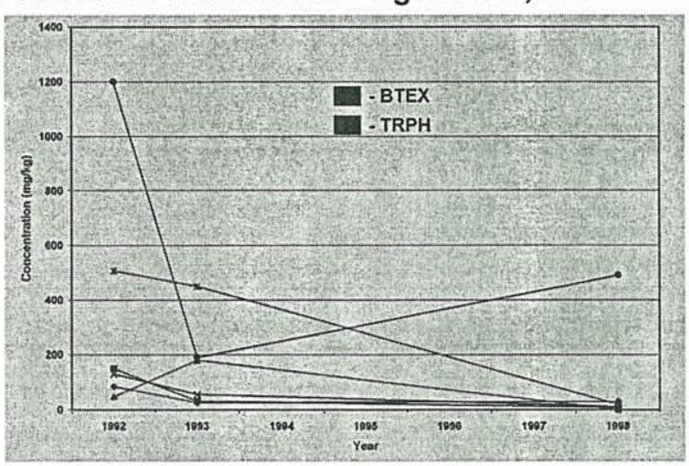
COPC	*Matrix*	*Units*	*Maximum Detection*	*Tier 1 RBSL*
Ethylbenzene	Soil	mg/kg	710	240
Xylenes (total)	Soil	mg/kg	1,400	290
Benzene	GW	µg/L	86	1
Toluene	GW	µg/L	11,000	40
Ethylbenzene	GW	µg/L	1,600	30
Xylenes (total)	GW	µg/L	13,000	20
Naphthalene	GW	µg/L	510	20
TRPH	GW	µg/L	38	5
Lead	GW	µg/L	19	15

Natural Attenuation Analysis

- Are COPCs naturally attenuating over time?
- What attenuation processes are significant?
- How much dissolved contaminant mass can be degraded?
- What are site-specific biodegradation rates for "risk-driver" chemicals?

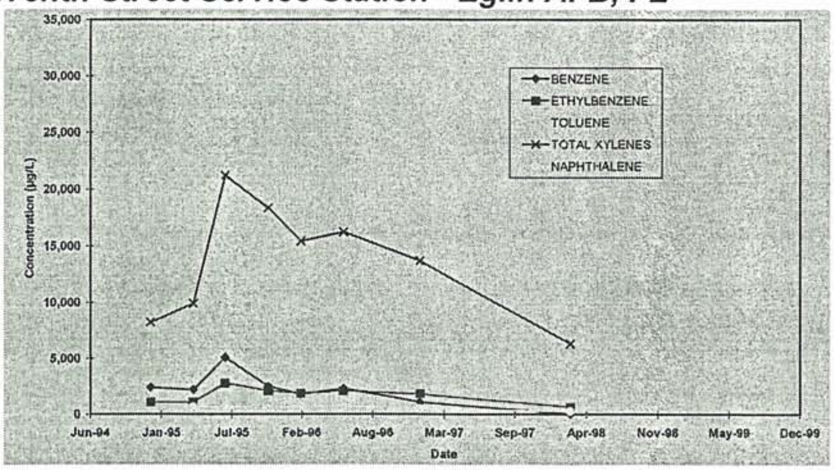
BTEX and TRPH in Soil Over Time

Seventh Street Service Station - Eglin AFB, FL



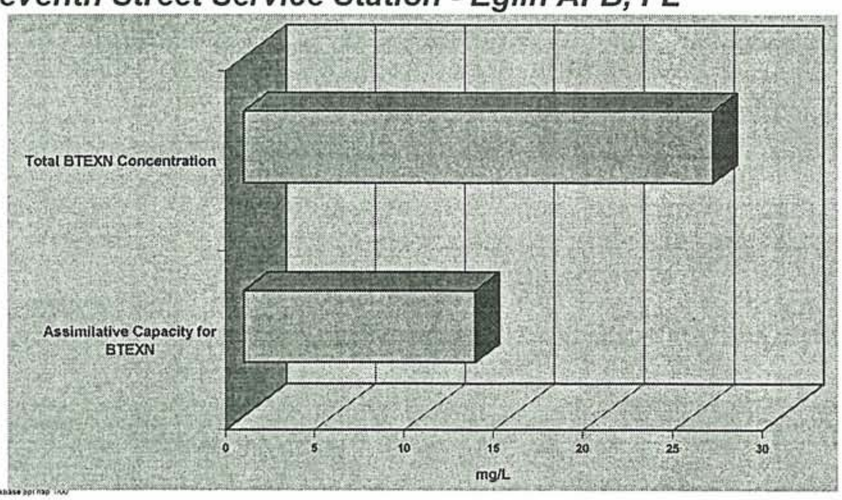
Dissolved COPC Concentrations vs Time at MW-2

Seventh Street Service Station - Eglin AFB, FL



Assimilative Capacity of Groundwater

Seventh Street Service Station - Eglin AFB, FL



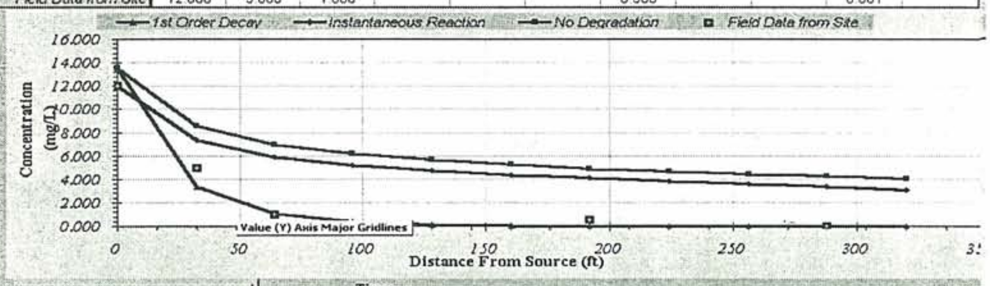
Biodegradation Rates for BTEX

Seventh Street Service Station - Eglin AFB, FL

Method	Rate (day^{-1})	Half-Life (year)
TMB Tracer	0.006	0.3
Busheck and Alcantar (1995)	0.01	0.2
Shrinking Plume Method	0.008	0.2

Bioscreen Output - Concentrations Along Plume Centerline

	Distance from Source (ft)										
TYPE OF MODEL	0	32	64	96	128	160	192	224	256	288	320
No Degradation	13.544	8.586	6.990	6.183	5.649	5.252	4.936	4.674	4.451	4.256	4.081
1st Order Decay	13.544	3.341	1.059	0.364	0.130	0.047	0.017	0.006	0.002	0.001	0.000
Inst. Reaction	12.021	7.387	5.927	5.208	4.742	4.302	4.101	3.841	3.595	3.352	3.000
Field Data from Site	12.000	5.000	1.000				0.500			0.001	



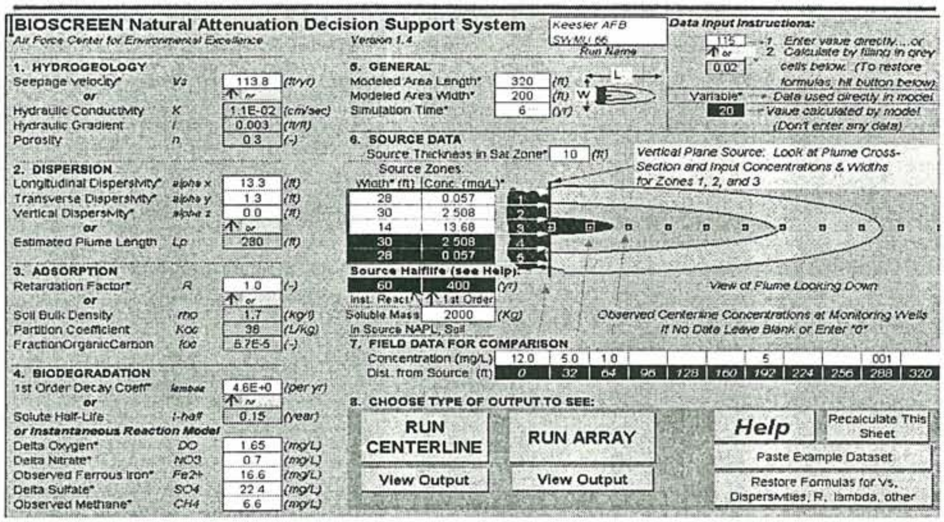
Calculate Animation

Time: 6 Years

Return to Input

Recalculate This Sheet

Bioscreen Input



BIOSCREEN Modeling Objectives for Eglin AFB

- **Estimate the max. migration distance of the plume assuming that the pump and treat and bioventing systems are not operating**
- **Assess plume persistence over time**
- **Support selection of remedial actions**
- **Simulated fate and transport of xylenes and benzene (2 remedial scenarios)**

BIOSCREEN Results

(Scenario 1-- No Engineered Remedial Action)

- **Xylene plume will migrate up to 950 feet from source area in 20 years, then recede**
- **Xylene plume will not reach Weekly Pond**
- **Maximum dissolved xylene concentration will be < Tier 1 RBSL within 150 years**
- **Benzene plume will not migrate to Weekly Pond**

BIOSCREEN Results

(Scenario 2-- 80% Source Removal in 3 Years)

- **Xylene plume will migrate up to 600 feet from source area within 10-15 years, then recede**
- **Maximum dissolved xylene concentration will be < Tier 1 RBSL within 30 years**

Tier 2 Comparison to SSTLS

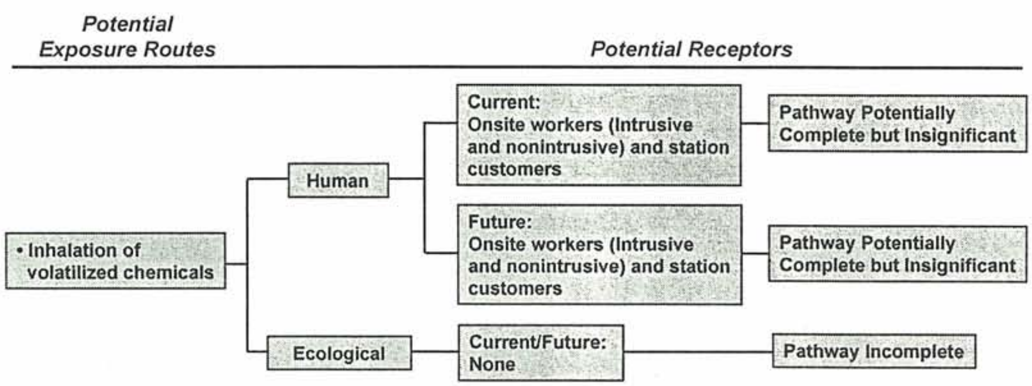
Seventh Street Service Station - Eglin AFB, FL

COPC	*Matrix*	*Units*	*Maximum Detection*	*Tier 2 Health-Based SSTL*	*Max. Detect Exceeds SSTL*
Ethylbenzene	Soil	mg/kg	710	240	No
Xylenes	Soil	mg/kg	1,400	290	No
Benzene	GW	µg/L	86	1	No
Toluene	GW	µg/L	11,000	40	No
Ethylbenzene	GW	µg/L	1,600	30	No
Xylenes (total)	GW	µg/L	13,000	20	No
Naphthalene	GW	µg/L	510	20	No

SSTL = Site-Specific Target Level

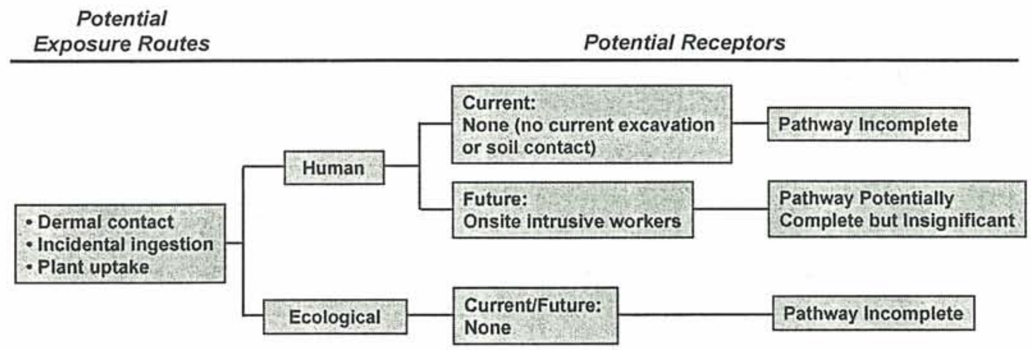
Conceptual Site Model for Air

Seventh Street Service Station - Eglin AFB, FL



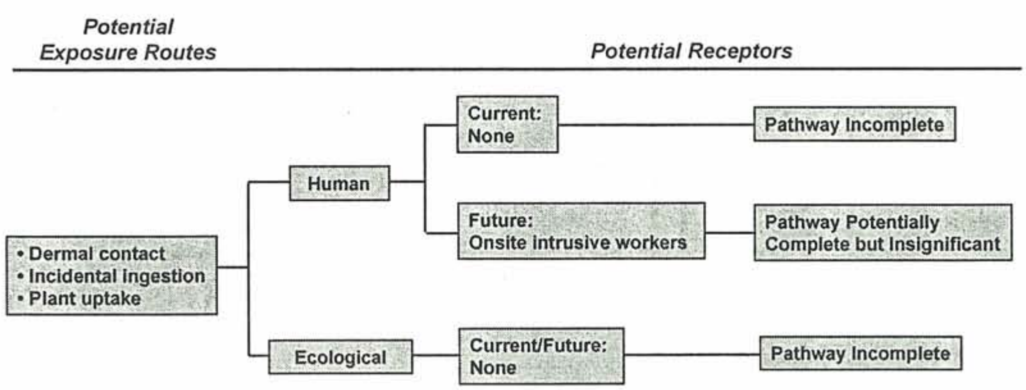
Conceptual Site Model for Soil

Seventh Street Service Station - Eglin AFB, FL



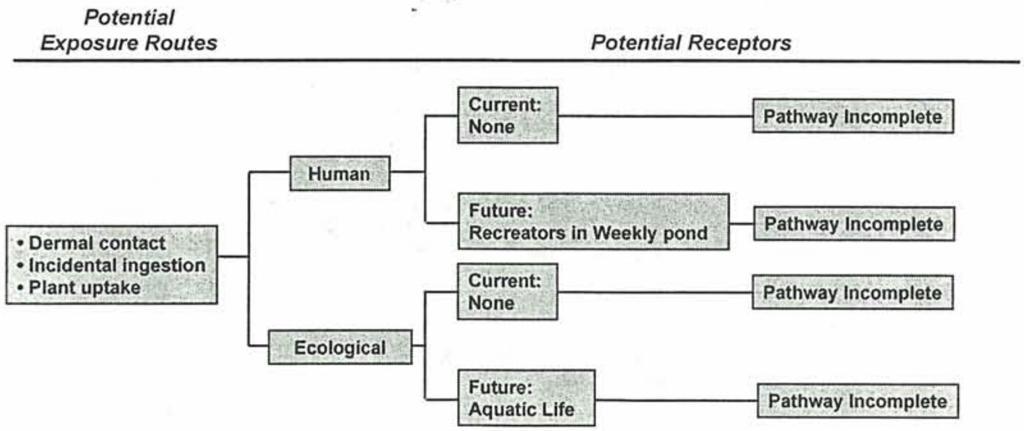
Conceptual Site Model for Shallow Groundwater

Seventh Street Service Station - Eglin AFB, FL

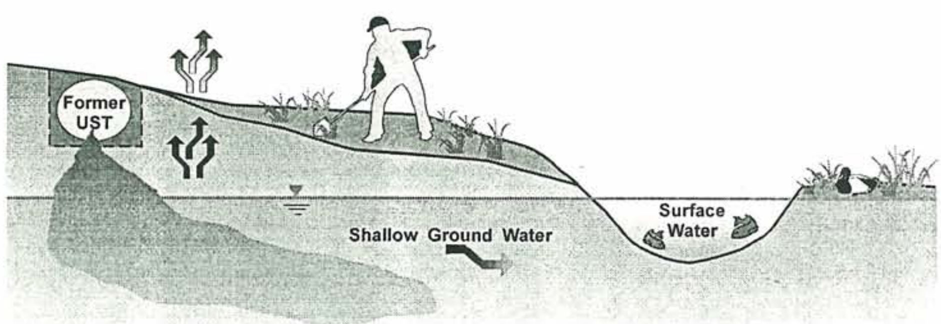


Conceptual Site Model for Surface Water

Seventh Street Service Station - Eglin AFB, FL

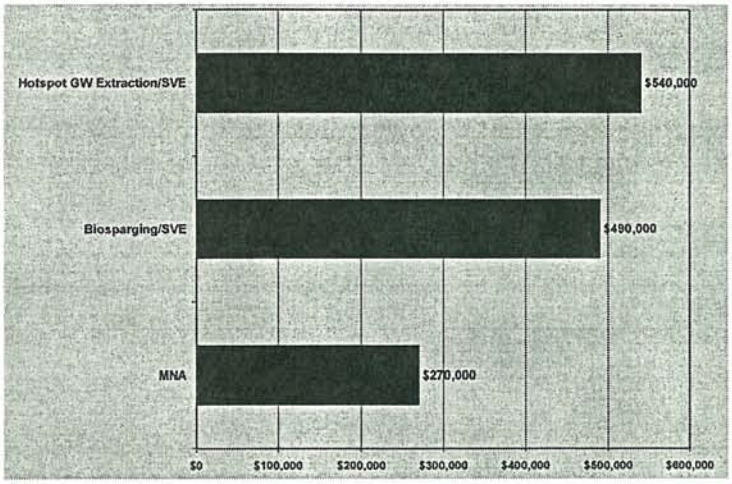


Conceptual Site Model



Remedial Alternatives Evaluation

Seventh Street Service Station - Eglin AFB, FL



Summary and Conclusions - Eglin AFB

- COPCs are biodegrading
- No significant risk to potential receptors
- Institutional controls can be maintained
- GW pumping not required to protect receptors
- COPCs in GW > RBSLs for >100 yrs unless engineered source reduction is performed
- Alternatives 2 or 3 will substantially accelerate cleanup

Recommendations and Site Status

Site	Recommendation	Status
Kelly AFB	Immediate Closure	Closure Granted
Randolph AFB	Conditional Closure	Conditional Closure
Keesler AFB	Conditional Closure	Conditional Closure
Eglin 7th St SS	MNA + Biosparging/SVE	Plan to Biosparge Source Area
Eglin Milgas	Conditional Closure	New Release-Return to Start
Tyndall BX SS	MNA	MNA +Source Reduction
Tyndall FT-16	Conditional Closure	Conditional Closure
Seymour Johnson	Product Recovery, then Closure	Product Recovery, then Closure
Pope AFB	No Recommendation	Regulatory Review

Average Streamlined RBCA Site Costs

	Average Cost Assuming Geoprobe® Rental and Subcontracted Drilling
Labor	$32,000
Other Direct Costs	$10,600
Project Management	$4,000
Average Cost per Site	$46,600

Lessons Learned

- Risk Assessment
  - know the State RBCA requirements
  - use up-to-date and defensible data and algorithms
  - analyze soil gas samples
- Value of Source Reduction
  - regulators more likely to accept MNA
  - reduces risks to future intrusive workers and allows lower level of institutional control

Lessons Learned (continued)

- Closure process for low-risk petroleum sites is being streamlined
- Feasible to perform entire RBCA process for <$50K per site
- Simple models acceptable to regulatory agencies
- Ability to limit exposure via institutional controls important

Methyl Tertiary-Butyl Ether (MTBE) Its Movement and Fate in the Environment and Potential for Natural Attenuation

PARSONS

PARSONS ENGINEERING SCIENCE, INC.

and the

Air Force Center for Environmental Excellence

Air Force Center For Environmental Excellence

Talk Based on *MTBE – Its Movement and Fate in the Environment and Potential for Natural Attenuation*

Technical Summary Report Prepared for AFCEE

Presents results of a comprehensive literature review of case histories of the fate of MTBE in the environment, and evaluate its potential for natural attenuation.

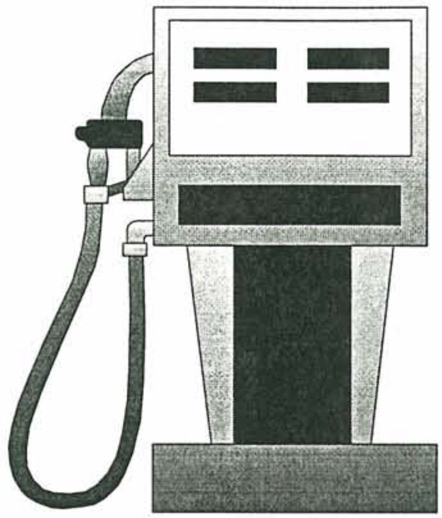
Presentation Outline

- Introduction
- Properties of Methyl *tertiary*-Butyl Ether (MTBE), and its Movement and Fate in the Environment
- Natural Attenuation Potential
- Methodology to Evaluate Natural Attenuation
- Considerations and Recommendations

What is MTBE ?

What is MTBE ?

- **Gasoline Additive**
  - **Increases octane**
  - **Oxygenates fuel**



mtbe ppt 1/2000 tw

Chemical Structure

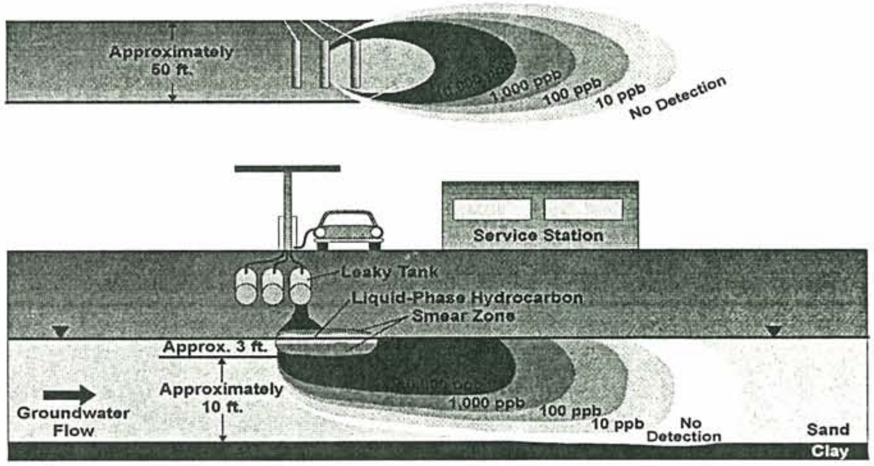
$$
\begin{array}{ccccccccc}
 & & CH_3 & & & & & & \\
 & & | & & & & & & \\
H_3 & — & C & — & C & — & O & — & CH_3 \\
 & & | & & & & & & \\
 & & CH_3 & & & & & &
\end{array}
$$

mtbe ppt 1/2000 tw

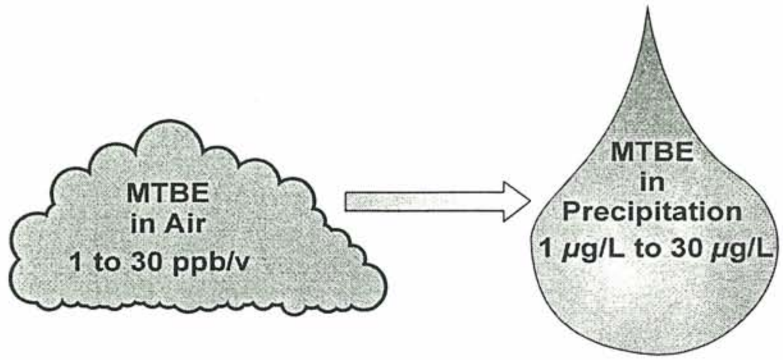
Sources of MTBE Contamination

- Point Sources (UST leaks, fuel spills)
  - typically high concentrations
  - 30 to 1,000,000 µg/L
- Non-point Sources (precipitation, runoff)
  - low concentrations
  - non-detect to 30 µg/L (typically < 5 µg/L)

UST Leak and Dissolved Hydrocarbon Plume



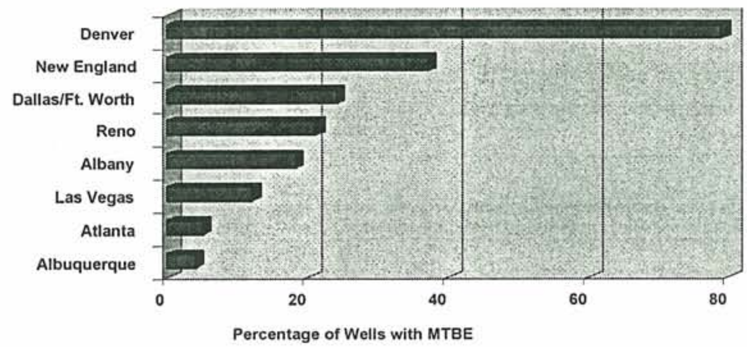
MTBE in Precipitation



USGS NWQA Program

- Second Most Common VOC detected
  - 210 urban wells sampled; 27% contained MTBE
- Concentrations
  - 73% < 0.2 μg/L
  - 24% from 0.2 to 20.0 μg/L
  - 3% > 20.0 μg/L

Frequency of MTBE Detection



mtbe ppt 1/2000 tw

What petroleum products can contain MTBE?

- Gasoline
- Aviation Fuel
- Jet Fuel
- Diesel
- Heating Oil
- Waste oil

Source: Kostecki and Leonard (1998)

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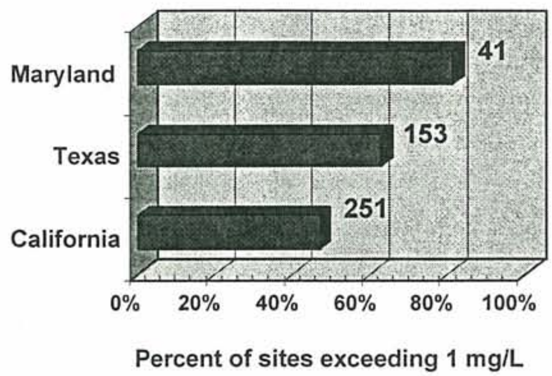
MTBE at UST Sites



T. Buscheck et al.,1998

Why is it a problem ?

- Recalcitrant nature
- Increasing regulation
- Chemical properties

Recalcitrant nature

- Conditions that favor biodegradation not well understood
- Slow biodegradation to nonexistent
- Few research studies

Increasing Regulation

- USEPA Drinking Water Advisory
  - 20 to 40 μg/L
- Standards in 25 States
  - Groundwater
  - Drinking water
  - Soil

mtbe ppt 1/2000 bw

Chemical Properties

- High Aqueous Solubility
  - 50,000 mg/L (MTBE) vs. 1,780 mg/L (benzene)
- Low Koc
  - 11.4 mL/g (MTBE) vs. 80 mL/g (benzene)
- Low Henry's Law Constant
  - ~ 0.02 (MTBE) vs. 0.22 (benzene)

Fate & Transport Mechanisms

- Advection
- Dispersion
- Sorption and Retardation
- Volatilization
- Biodegradation

Chemical Characteristics of MTBE that Affect its Movement and Fate in the Environment

- Solubility
- Volatility
- Partitioning (fuel, air, water, sorbed phases)

Compare MTBE with Benzene

- Benzene
  - Typical contaminant of concern
  - MCL -- 5 µg/L
  - Known toxic effects (carcinogen)
- MTBE
  - Also often found associated with fuel spills
  - Safe Drinking Water Act Candidate List
  - Drinking-water advisory -- 20 - 40 µg/L
  - Standard based on taste & odor threshold

Compare MTBE with Benzene

- Vapor Pressure
  - MTBE = 200 mm Hg @ 20° C
  - Benzene = 76 mm Hg @ 20° C

Conclusion:
MTBE more volatile from the chemical phase to the vapor phase.

Compare MTBE with Benzene

- Aqueous Solubility of Pure Phase
  - 50,000 mg/L (MTBE) vs. 1,800 mg/L (benzene)

Conclusion:
MTBE is ~30 times more soluble than benzene

Effective Aqueous Solubility

$$S_i^e = \gamma_i \cdot X_i \cdot S_i^o$$

(describes dissolution of constituent from fuel)

γ_i = 1.1

X_i = mole fraction ($\approx$ volume fraction)

$S_i^o \approx$ 50,000 mg/L (solubility from pure phase)

$S_i^e \approx$ 5,000 mg/L (MTBE; ~15% by volume)

$S_i^e \approx$ 50 mg/L (benzene; ~3% by volume)

mtbe ppt 1/2000 tw

Fuel-Water Partition Coefficient

$$K_{fw} = \frac{\text{concentration in gasoline (mg/L)}}{\text{concentration in water (mg/L)}}$$

(describes tendency of a constituent to partition from fuel to water)

- MTBE K_{fw} = 15.5
- Benzene K_{fw} = 350

Conclusion:

MTBE partitions out of the fuel phase and into the aqueous phase much more readily than benzene

mtbe ppt 1/2000 tw

Henry's Law Constant

$$H = \frac{\text{concentration in air}}{\text{concentration in water}}$$

(describes tendency of constituent to partition between aqueous and vapor phases)

- 0.02 (MTBE) vs. 0.2 (benzene)
- MTBE is 10 times less volatile from aqueous phase

Conclusion:

MTBE prefers the aqueous phase

Soil-Water Partition Coefficient

$$K_d = \frac{\text{sorbed concentration}}{\text{aqueous concentration}} = f_{oc} \text{ X } K_{oc}$$

(describes relative tendency of dissolved constituent to partition between the sorbed and aqueous phases; depends on fraction of organic carbon in soil [f_{oc}] and chemical organic-carbon partition coefficient [K_{oc}])

- Koc = 11 mL/g (MTBE)
- Koc = 80 mL/g (benzene)

Conclusion:

MTBE partitions to soil much less than does benzene

Retardation Factor

$$R = 1 + (\rho_b \times K_d)/\, n$$

(ratio between migration velocity of dissolved constituent and groundwater flow velocity)

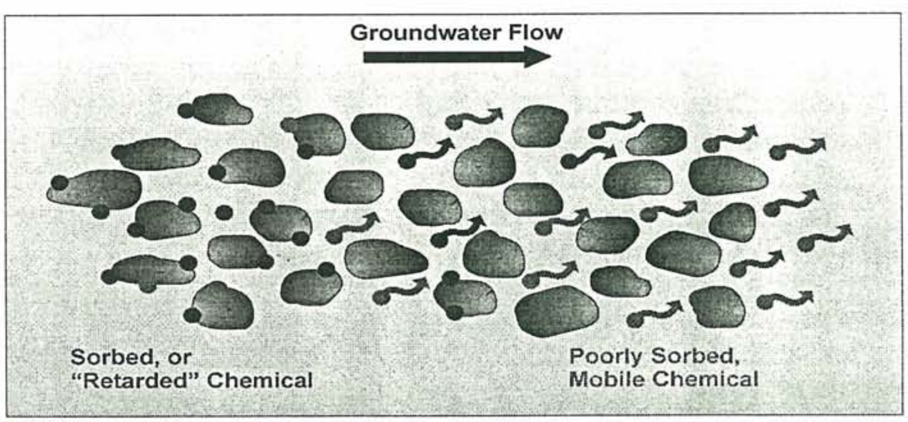
Representative Values of Retardation:

- **R = 1.05 (MTBE)**
- **R = 1.6 (benzene)**

Conclusion:

MTBE velocity ≈ groundwater velocity

Chemical Retardation and Dispersion



Bottom Line

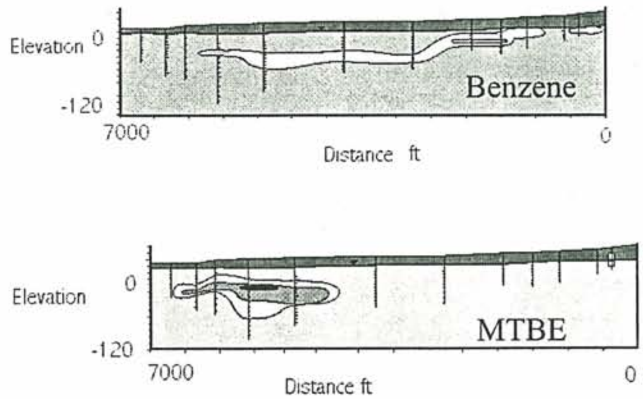
- MTBE is Much More Mobile and Persistent in Groundwater than BTEX
- MTBE Tends to Leach out of Source Areas Faster than BTEX, thus it will Leave the Source Area Sooner

Example of MTBE Fate & Transport

- East Patchogue NY, gasoline spill *
  - USEPA site
  - 3-D monitoring network
  - Abandoned USTs
  - MTBE migration about 6,000 feet from source -- 1,500 feet further than benzene
  - Source depleted in MTBE

  * Weaver *et al.*, 1996

Contaminant Distribution 1995

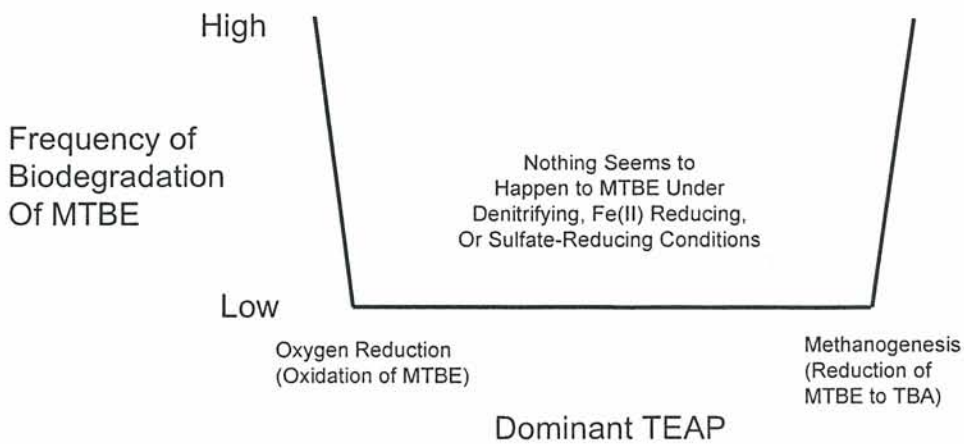


after Weaver *et al.*, 1996

Biodegradation of MTBE

- **Not well Documented (few case histories)**
- **Usually Slow when it does Occur**
- **Typically Occurs under Aerobic or Strongly Anaerobic (typically methanogenic) Conditions**
- **Under Aerobic Conditions "Oxidized"**
- **Under Strongly Anaerobic (methanogenic) Conditions "Reduced"**

Susceptibility of MTBE to Biodegradation



MTBE Attenuation Processes

- **MTBE Seems to be Biologically Recalcitrant at Many Sites**
- **MTBE is generally not retarded, and moves with advective groundwater flow**
- **MTBE is not readily volatilized from water**
- **Therefore, *dispersion may be the predominant natural attenuation process***

Methods of Evaluating Natural Attenuation

- Demonstrate loss of mass or reduction in concentration at field scale
- Spatial and temporal association of changing contaminant concentrations and geochemical indicators (O_2, NO_3^-, SO_4^{--}, Fe^{++}, CH_4)
- Direct microbiological evidence

Considerations for Site Characterization

- MTBE may be a constituent of any petroleum fuel
- MTBE may become rapidly depleted in source areas, but persist in downgradient areas
- MTBE migrates more rapidly, and to greater distances, than BTEX compounds
- MTBE and daughter products may not be detected at low concentrations, using certain analytical methods (SW8020/8021)

Considerations for Site Characterization (continued)

- Geochemical indicators of BTEX and MTBE biodegradation are the same -- MTBE biodegradation may be difficult to distinguish from BTEX biodegradation
- Principal anaerobic degradation product of MTBE (TBA) is also used as a fuel oxygenate -- its appearance is not conclusive evidence of biodegradation

Recommendations

- MTBE plumes and BTEX plumes may separate
- MTBE plumes may not stabilize at short distances from source
- Because of its Solubility, MTBE is Rapidly Depleted from the Source
- If Present, Monitoring locations should be selected with MTBE properties in mind

Recommendations (continued)

- Use appropriate methods of chemical analyses [SW8260; DAI-GC/MS Method of Church *et al.* (1997)]
- Attempt to distinguish degradation from dispersion:
  - Mass balance/mass flux estimates
  - Use tracer to estimate site-specific value of dispersivity

Recommendations (concluded)

- Properly-constructed microcosms may provide best site-specific evidence of MTBE biodegradation; may be time-consuming and expensive and certainly not something that AFCEE should undertake

mtbe ppt 1/2000 tw

Weathering of JP-4 LNAPL Hydrocarbons and Implications for Risk-Based Site Closures and Monitored Natural Attenuation

Presented by

Bruce Henry

PARSONS
PARSONS ENGINEERING SCIENCE, INC.

Introduction

This presentation presents the results of work completed to evaluate natural weathering of light nonaqueous-phase liquids (LNAPLs) resulting from petroleum releases to the subsurface environment. Of particular interest for this study was the weathering, or natural depletion, of benzene, toluene, ethylbenzene, and xylenes (BTEX) from free-phase product (i.e., mobile LNAPL) following a JP-4 jet fuel release.

Problem Statement

Little information is available regarding natural weathering rates of the BTEX components from mobile fuel LNAPLs. As a result, contaminant source-term reduction rates in groundwater models are left to professional judgment, with little, or no, basis.

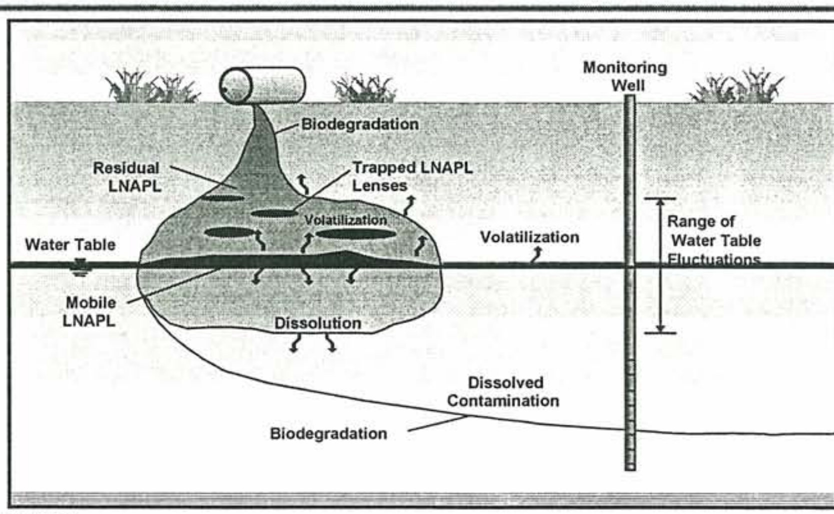
Implications

- **Overly conservative LNAPL weathering rates negatively impact feasibility and cost of implementing monitored natural attenuation (MNA).**
- **Overestimation of weathering rates can lead to an overly optimistic forecast of MNA performance.**
- **A default value of 5 percent per year (%/yr) often has been assumed, but with no scientific validation.**

Project Objective

Improve the scientific basis of, and defensibility for, natural LNAPL weathering rates (i.e., contaminant source-term reduction rates).

LNAPL Weathering Conceptual Model



LNAPL Weathering Mechanisms

- The primary mechanisms acting to reduce the strength of the LNAPL source are:
  - Dissolution
  - Volatilization
  - Biodegradation
- These mechanisms are influenced by physical and chemical properties of the compounds in the source product, as well as by physical, chemical, and biological properties of the soil and groundwater system.

Site Selection Criteria

Identifying sites that met all of the criteria listed below proved to be difficult; therefore, the criteria were used as guidelines for site selection:

1. Presence of recoverable mobile JP-4 LNAPL in the subsurface
2. Known date of fuel release
3. Single release confined to a relatively short period of time

Site Selection Criteria (continued)

4. Minimal site remediation
5. Historic LNAPL analytical results for BTEX
6. Depth to groundwater less than 40 feet bgs
7. DOD sites

JP-4 Release Site Summary

Five JP-4 sites, with spill ages ranging between approximately 4 and 24 years, were included in the study.

Site/Location	*Date of Release*	*Amount Released (gallons)*	*Soil Type*
Bldg 1610 Shaw AFB, SC	June 1994	Unknown	Sand
Pipeline Leak Site Myrtle Beach AFB, SC	January 1981	123,000	Clay/Sand
Tank 1 Area, DFSP Charleston, Hanahan, SC	October 1975	83,000	Clay/Sand
Spill Site No. 2 Eaker AFB, AR	October 1973	Unknown	Sandy Silt
Washrack/Treatment Area McChord AFB, WA	1975	100,000	Silty Gravel

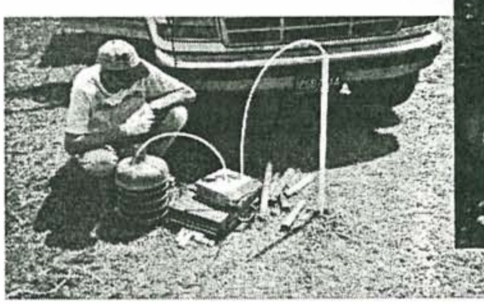
bmhweathering.ppt 1/2000

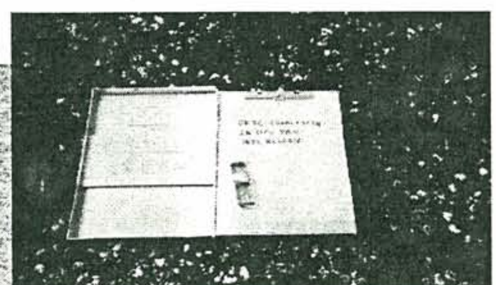
JP-4 Release Site Summary (continued)

Five JP-4 sites, with spill ages ranging between approximately 4 and 24 years, were included in the study.

Site/Location	*Depth to Water Table (feet bgs)*	*Groundwater Velocity (feet/year)*	*Free Product Thickness (feet) and Date*
Bldg 1610 Shaw AFB, SC	29-33	400	2.5 (8/96)
Pipeline Leak Site Myrtle Beach AFB, SC	2-8.5	420	3.79 (11/95)
Tank 1 Area, DFSP Charleston, Hanahan, SC	18-22	62	1.77 (5/96)
Spill Site No. 2 Eaker AFB, AR	8-14	16	1.18 (8/97)
Washrack/Treatment Area McChord AFB, WA	11-15	NA	0.14 (4/94)

Sample Collection and Analysis



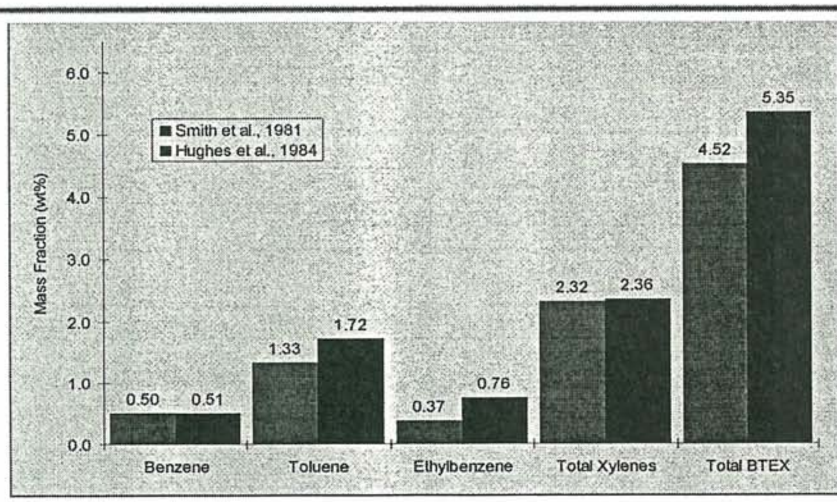


Soil, groundwater, and LNAPL samples were collected and analyzed for BTEX and naphthalene

BTEX Weathering in JP-4 LNAPL

- To estimate weathering rates, the following must be known:
  - Initial BTEX concentrations in fresh JP-4
  - Date of fuel release
  - Date of sampling event

BTEX Composition in Fresh JP-4



Individual Site Data

- **Using the known dates of the product release and the assumed initial BTEX composition, the degree of mobile LNAPL weathering (i.e., BTEX mass fraction depletion) that has occurred with time was determined for each release site.**
- **Minimum, maximum, and average annual contaminant reduction rates, assuming zero-order and first-order weathering at the five JP-4 sites, were calculated.**

Site Specific BTEX Weathering Rates in JP-4 Mobile LNAPL

Site Analyte	*Approximate Spill Age*	*Zero Order (%yr)*			*First Order (%yr)*		
		min	max	avg	min	max	avg
Shaw AFB, SC **Total BTEX**	**4 years**	**14**	**24**	**18**	**16**	**33**	**23**
Myrtle Beach AFB, SC **Total BTEX**	**16 years**	**4.6**	**5.7**	**5.1**	**8.3**	**14**	**11**
DFSP-Charleston, SC **Total BTEX**	**22 years**	**3.7**	**5.2**	**4.3**	**6.7**	**18**	**11**
Eaker AFB, AR **Total BTEX**	**24 years**	**0.0**	**3.3**	**1.7**	**0.0**	**6.1**	**2.9**
McChord AFB, WA **Total BTEX**	**22 years**			**4.5**			**43**

Site Specific Benzene Weathering Rates in JP-4 Mobile LNAPL

Site Analyte	Approximate Spill Age	Zero Order (%yr) min	Zero Order (%yr) max	Zero Order (%yr) avg	First Order (%yr) min	First Order (%yr) max	First Order (%yr) avg
Shaw AFB, SC Benzene	4 years	11	23	17	12	31	22
Myrtle Beach AFB, SC Benzene	16 years	5.8	6.1	5.9	16	23	19
DFSP-Charleston, SC Benzene	22 years	4.6	5.5	4.8	14	43	35
Eaker AFB, AR Benzene	24 years	2.0	4.2	3.1	2.7	26	12
McChord AFB, WA Benzene	22 years			4.5			42

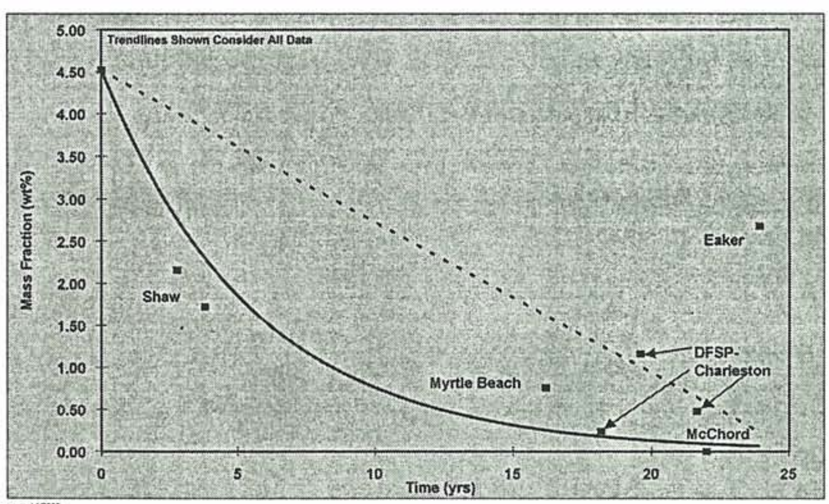
Site Specific BTEX Weathering Rates in JP-4 Mobile LNAPL

- No BTEX was detected in the one LNAPL sample from the McChord AFB site.
- Low reduction rates at the Eaker AFB site likely are the result of a more recent, undocumented, fuel release.

Combine JP-4 Site Data to Assess Weathering Rates

- **Data from all five JP-4 sites were compiled to evaluate the relationship between BTEX depletion in mobile JP-4 LNAPL and spill age.**
- **Calculate total BTEX and benzene weathering considering average data from the JP-4 release sites**

Total BTEX Weathering Considering Average Data



Total BTEX Weathering Considering All Data

Zero-Order

Best Fit Curve: $y = -0.1795x + 4.52$

$R^2 = 0.0248$

Weathering Rate = 4.0%C_o per year

First-Order

Best Fit Curve: $y = 4.52e^{-0.1783x}$

$R^2 = 0.1829$

Weathering Rate = 16.3% per year

Total BTEX Weathering Considering All Data Except Eaker

Zero-Order

Best Fit Curve: $y = -0.2095x + 4.52$

$R^2 = 0.4428$

Weathering Rate = 4.6%C_o per year

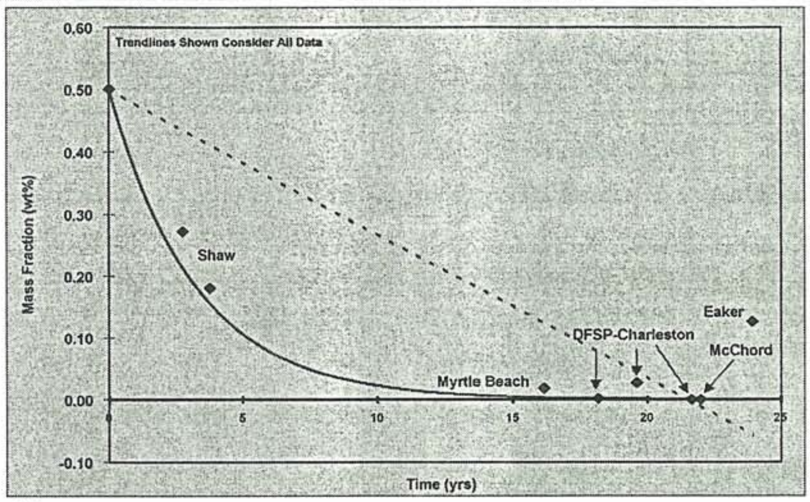
First-Order

Best Fit Curve: $y = 4.52e^{-0.2242x}$

$R^2 = 0.3104$

Weathering Rate = 20% per year

Benzene Weathering Considering Average Data



Benzene Weathering Considering All Data

Zero-Order

Best Fit Curve: $y = -0.0233x + 0.50$

$R^2 = 0.4368$

Weathering Rate = 4.7%C_o per year

First-Order

Best Fit Curve: $y = 0.50e^{-0.3099x}$

$R^2 = 0.4063$

Weathering Rate = 26.7% per year

Benzene Weathering Considering All Data Except Eaker

Zero-Order

Best Fit Curve: $y = -0.0255x + 0.50$

$R^2 = 0.6221$

Weathering Rate = $5.1\% C_o$ per year

First-Order

Best Fit Curve: $y = 0.50e^{-0.3839x}$

$R^2 = 0.6548$

Weathering Rate = 31.9% per year

Dissolution Dominated Weathering

- **As mobile LNAPL concentrations decrease, compound depletion rates decrease (in accordance with Raoult's Law).**
- **Benzene and toluene weathering rates generally are higher than ethylbenzene and xylene weathering rates (because of their higher effective water solubilities).**

Dissolution Dominated Weathering (continued)

- **Under equilibrium conditions, lower groundwater velocities create a lower dissolution flux for mobile LNAPL depletion.**
  - **The lowest weathering rates were observed at the Eaker AFB site (groundwater velocity approximately 16 feet per year).**
  - **Higher BTEX depletion rates were observed at the other sites possibly because of higher groundwater velocities and/or precipitation rates.**

Conclusions

1. **BTEX weathering rates in free-phase fuel, or mobile LNAPL, will vary from site to site and are influenced by:**
   - **Spill age**
   - **Solubility and LNAPL concentration of individual compounds**
   - **Free product geometry**
   - **Groundwater and precipitation rates**

Conclusions (continued)

2. The BTEX fraction remaining in free-phase LNAPL samples collected from different locations on the same site will vary.
   - Samples from the center of the LNAPL "plume" will exhibit lower rates of weathering
   - A site average based on multiple samples is recommended

Conclusions (continued)

3. Weathering of BTEX from LNAPL is expected to follow first-order kinetics in accordance with Raoult's Law
4. Average first-order total BTEX weathering in JP-4 mobile LNAPL
   - Range: 11 – 23%/yr (excluding McChord and Eaker data)
   - Recommended default: 16%/yr
   - Conservative default: 11%/yr

Conclusions (continued)

5. Because benzene is a known human carcinogen with a federal MCL of 5 µg/L, benzene weathering rates will generally determine the timeframe for fuel spill remediation.

6. Average first-order benzene weathering in JP-4 mobile LNAPL

- **Range: 19 – 35%/yr (excluding McChord and Eaker data)**
- **Recommended default: 26%/yr**
- **Conservative default: 19%/yr**

Conclusions (concluded)

7. Dissolution appears to be the primary weathering mechanism that influences mobile LNAPL weathering rates. Significantly lower BTEX weathering rates in mobile LNAPL were apparent at sites with low groundwater velocities.

Source Reduction Effectiveness Technical Summary Report

Presented by

John R. Hicks

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PARSONS ENGINEERING SCIENCE, INC.

Presentation Outline

- **Project Objectives and Site Locations**
- **Statistical Tools**
- **Case Histories**
- **Summary and Conclusions**

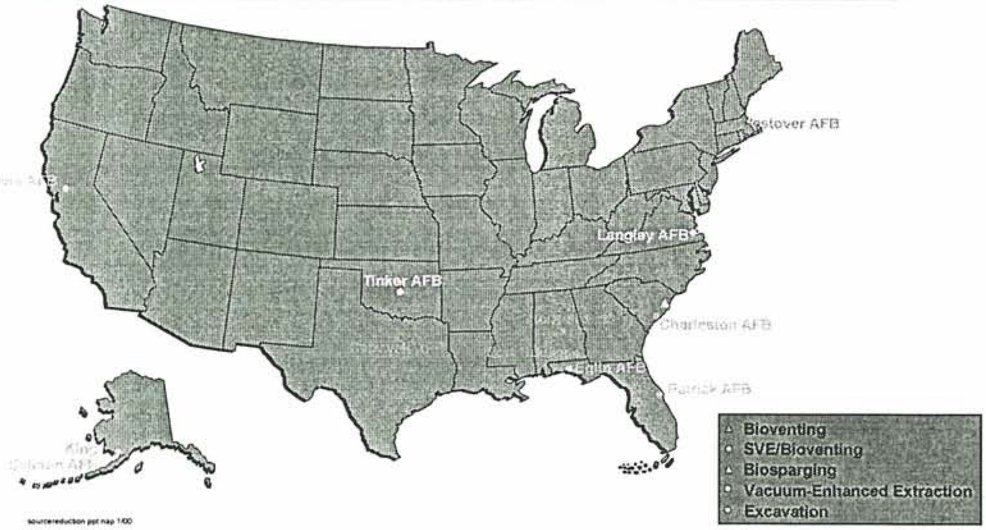
Project Description and Objectives

- Assess the degree to which various types of engineered source-reduction efforts at selected fuel-contaminated sites have resulted in decreasing concentrations of fuel constituents dissolved in groundwater; and

Project Description and Objectives

- Describe a methodology for evaluating the potential effectiveness of source-reduction actions at reducing the magnitude and extent of dissolved fuel constituents

Source Reduction Sites

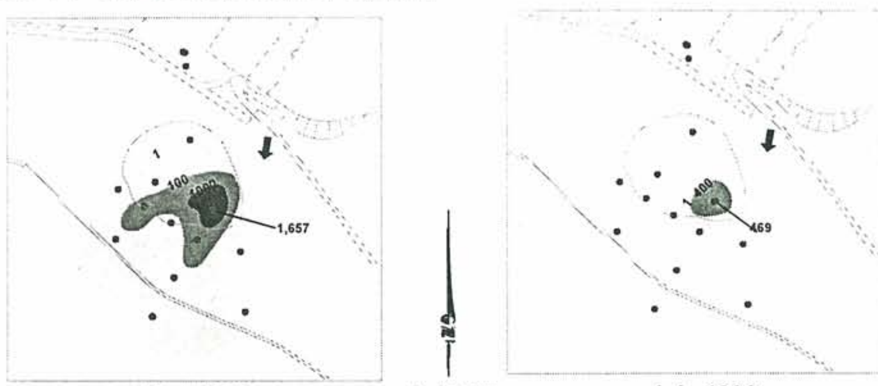


Statistical Tools

- Mann-Kendall Test for Trend
  - nonparametric
  - non-detects can be used
  - requires only small sample sizes
- Sen's Nonparametric Estimator of Slope
  - not greatly affected by outliers
  - magnitude of slope is indicator of rate of change

BTEX in Groundwater

Site FT-03, Westover AFB, MA



May 1975

July 1996

>1000 µg/L 100-1000 µg/L 1-100 µg/L

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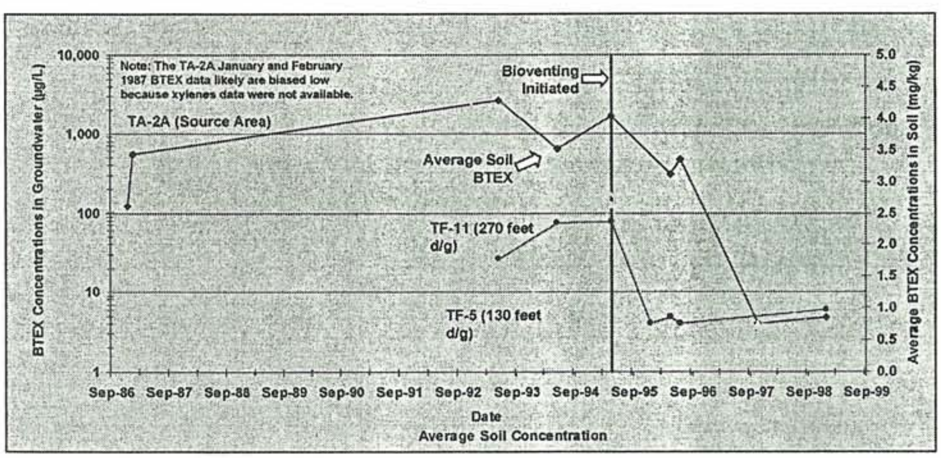
BTEX Concentrations in Groundwater and Soil

Site FT-03 - Westover AFB, MA



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Statistical Summary for BTEX

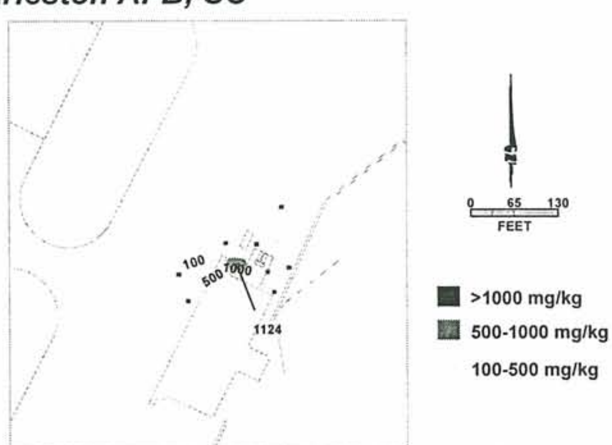
Site FT-03 - Westover AFB, MA

Well Location	Pre-Remed MK	Post-Remed MK	Pre-Remed Slope	Post-Remed Slope	Pre-Remed BTEX µg/L	Most recent BTEX µg/L
Source	-1	-6	-520	-323	1,657 (0.0 yr)	4.9 (3.7 yr)
130 feet d/g	1	0	46	0	124 (0.0 yr)	6 (3.7 yr)
270 feet d/g	3	-1	25	-0.4	77 (0.0 yr)	<6 (3.7 yr)

220 ft/yr.

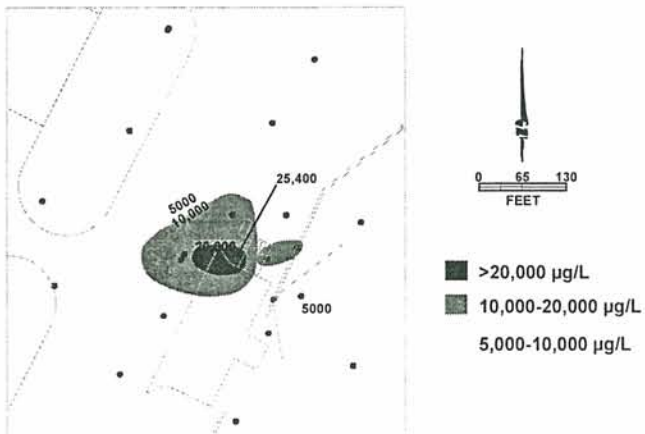
Soil BTEX Concentrations, 4'-6' BGS

Site ST-27, Charleston AFB, SC



BTEX in Groundwater, 1995

Site ST-27, Charleston AFB, SC



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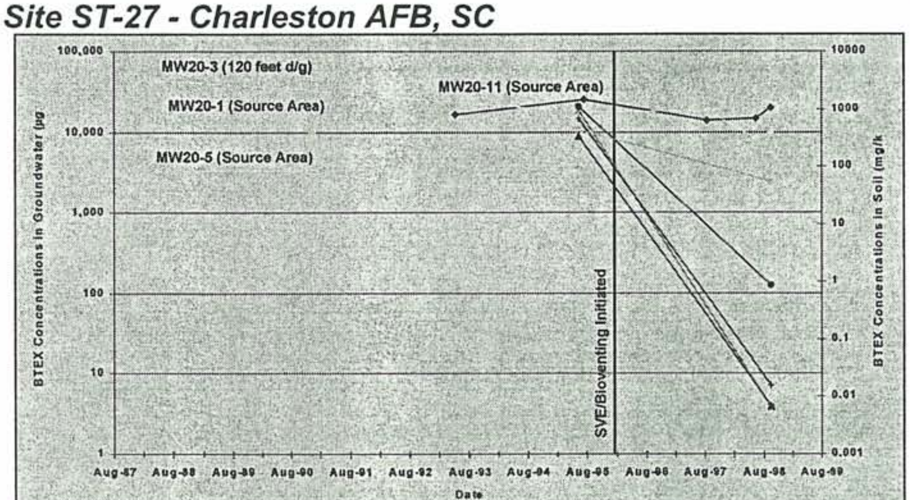
BTEX Concentrations in Groundwater and Soil

Site ST-27 - Charleston AFB, SC



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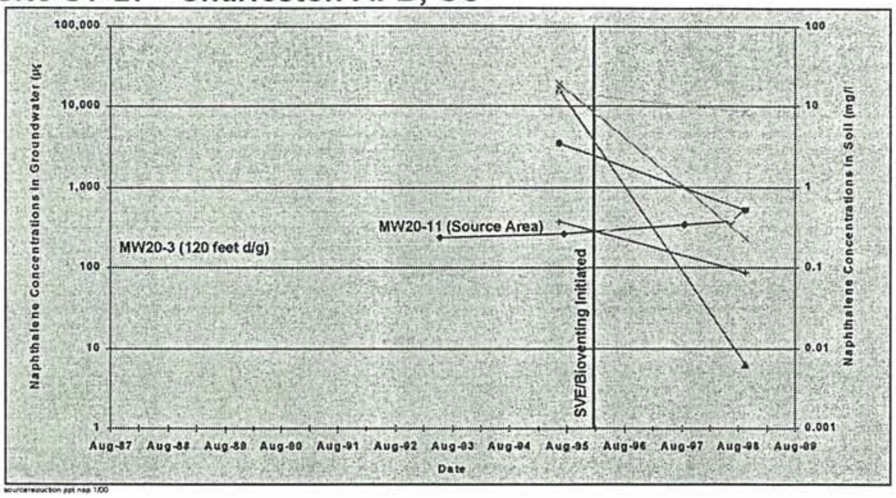
Naphthalene Concentrations in Groundwater

Site ST-27 - Charleston AFB, SC



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Statistical Summary for BTEX

20ft/yr

Site ST-27 - Charleston AFB, SC

Well Location	*Pre-Remed MK*	*Post-Remed MK*	*Pre-Remed Slope*	*Post-Remed Slope*	*Pre-Remed BTEX µg/L*	*Most recent BTEX µg/L*
Source	-3	-1	-971	-368	1,481 (0.5 yr)	746 (2.7 yr)
120 feet d/g	-3	-2	-13,065	-3,372	17,500 (0.5 yr)	9,888 (2.7 yr)

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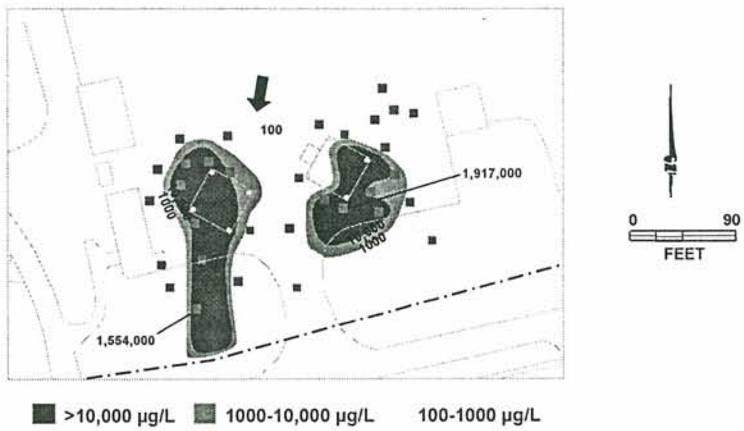
Soil BTEX Concentrations - 1988-1995

MOGAS Site - Myrtle Beach AFB, SC



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Air Sparging System Layout

MOGAS Site - Myrtle Beach AFB, SC

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Benzene in Groundwater

MOGAS Site - Myrtle Beach AFB, SC

August/September 1995

August/October 1999

>1000 µg/L 100-1000 µg/L 10-100 µg/L 1-10 µg/L

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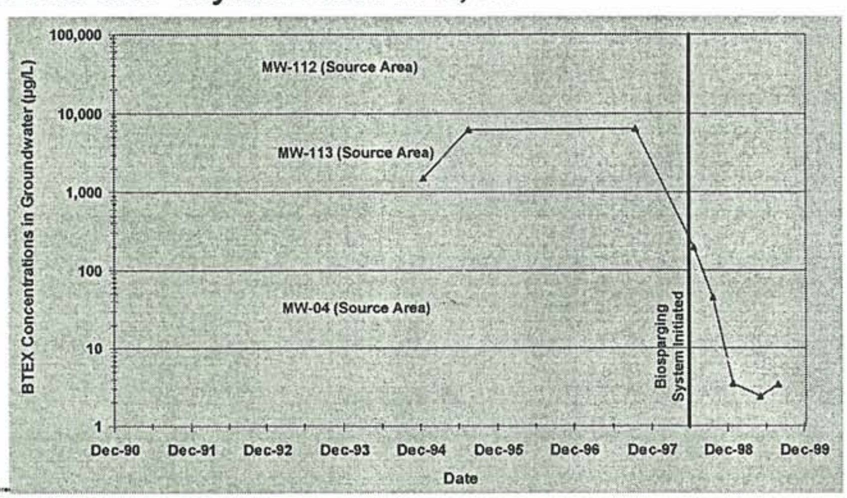
BTEX Concentrations in Groundwater

MOGAS Site - Myrtle Beach AFB, SC



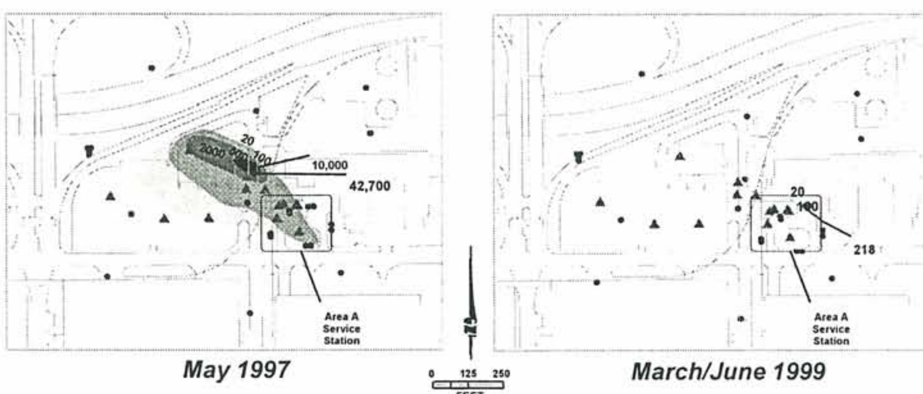
Statistical Summary for BTEX

MOGAS Site - Myrtle Beach AFB, SC

Well Location	*Pre-Remed MK*	*Post-Remed MK*	*Pre-Remed Slope*	*Post-Remed Slope*	*Pre-Remed BTEX µg/L*	*Most recent BTEX µg/L*
Source	1	-2	498	-2,422	43,100 (0.5 yr)	160 (1.3 yr)
Source	3	-8	2,424	-32	6,380 (0.5 yr)	3 (1.3 yr)
Source	3	-8	91	-4	194 (0.5 yr)	5 (1.3 yr)

BTEX in Groundwater

Area A Service Station - Tinker AFB, OK

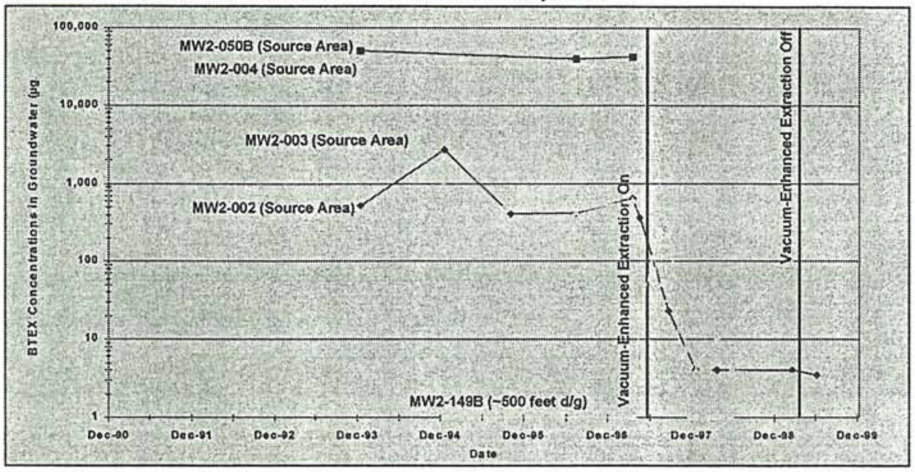


May 1997 *March/June 1999*

>10,000 µg/L 2000-10,000 µg/L 500-2000 µg/L 100-500 µg/L 20-100 µg/L

BTEX Concentrations in Groundwater

Area A Service Station - Tinker AFB, OK



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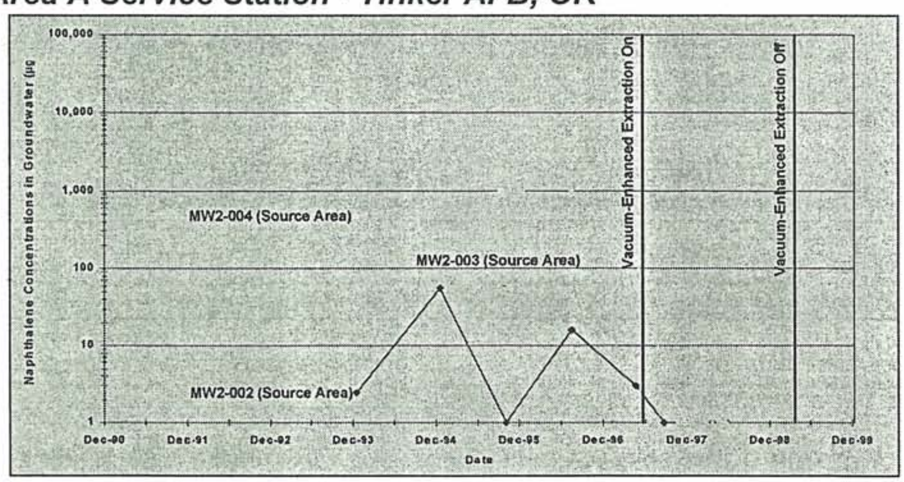
Naphthalene Concentrations in Groundwater

Area A Service Station - Tinker AFB, OK



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Statistical Summary for BTEX

Area A Service Station - Tinker AFB, OK

Well Location	Pre-Remed MK	Post-Remed MK	Pre-Remed Slope	Post-Remed Slope	Pre-Remed BTEX µg/L	Most recent BTEX µg/L
Source	-2	-4	-1,925	-4,433	26,150 (0.1 yr)	217 (2.2 yr)
Source	-5	-3	-33	-178	359 (0.1 yr)	4 (2.2 yr)
20 feet d/g	-7	-9	-101	-42	618 (0.1 yr)	4 (1.9 yr)

Summary and Conclusions

- Careful site characterization prior to selection of remedial method
- Borehole advancement below the water table
- Assessment of smear zone thickness

Bioventing and SVE

- Primary factor = smear zone presence
- Smear zone persistence = plume persistence
- Mounding of water table at SVE sites
- Charleston AFB Site ST-27--less effective

Biosparging

- Potential for smear zone remediation
- Sandy, homogeneous soils
- Rapid decreases of dissolved BTEX with depth
- Well spacing <= 20 feet
- Myrtle Beach AFB - rate increase of 101-586%

Vacuum-Enhanced Extraction

- Aggressive method
- Thin saturated zones
- Low- to moderate-permeability soils
- Presence of free product

Vacuum-Enhanced Extraction

- Dewatering of smear zone
- Tinker AFB Area A success
- 130 to 439 % increase in BTEX removal rates

Excavation

- Effectiveness on dissolved contamination function of thoroughness of excavation
- Excavation below the water table can be problematic
- Mixed success at Travis AFB N & S Gas Stations

Additional Fuel Compounds

- Naphthalene
- MTBE

Naphthalene

- Source reduction less effective
- Charleston AFB
  - increasing concentrations following SVE/Bioventing
- Eglin and Myrtle Beach AFBs
  - 75 to 99 % slower than BTEX reductions

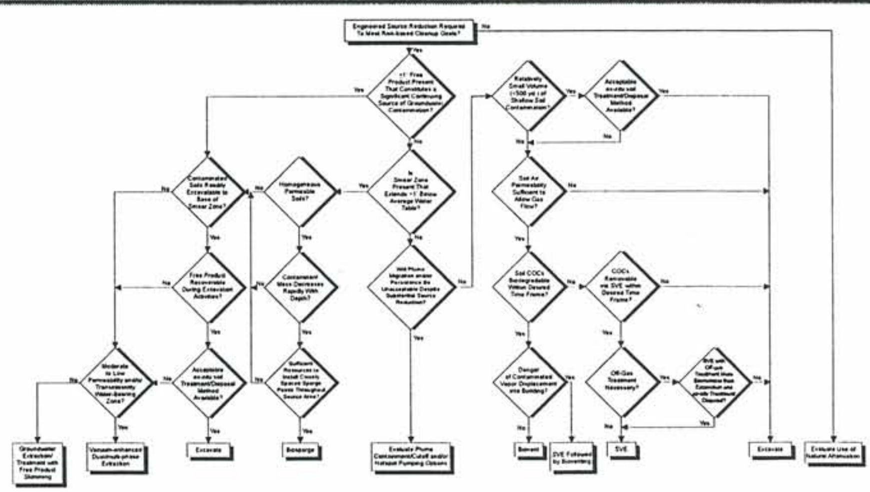
Naphthalene

- Lower volatility
- More recalcitrant to biodegradation
- Higher degree of sorption
- More success at Tinker AFB Area A

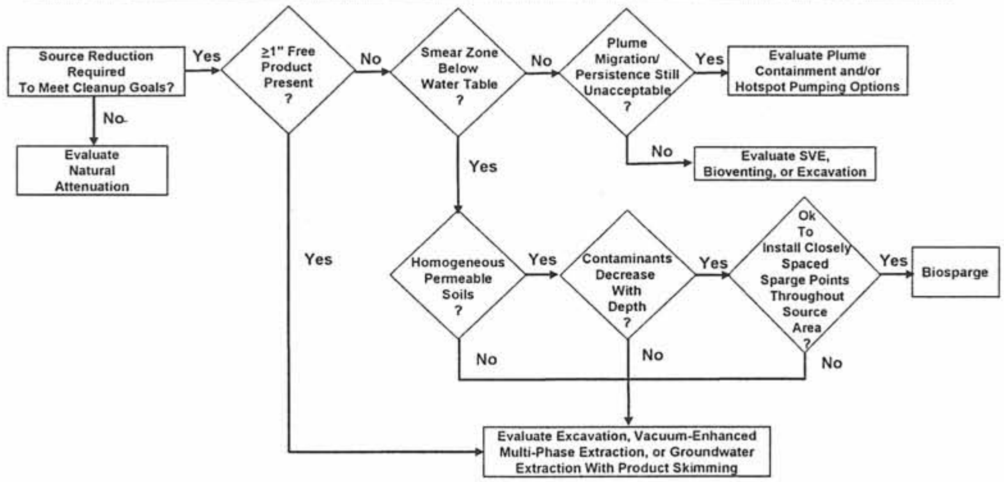
MTBE

- Travis AFB
  - 54 to 95 % slower than BTEX reductions
- Vadose zone source removal less likely to cause rapid reductions in dissolved concentrations
- Can be relatively recalcitrant
- Quickly leaches from soil

Methodology for Selecting an Engineered Source Reduction Technique



Methodology for Selecting an Engineered Source Reduction Technique



Future Directions for Natural Attenuation

- **Integration with Active Remediation**
  - **The Role of Natural Attenuation in Remedial Process Optimization**
- **Enhanced Bioremediation**

Remedial Process Optimization

Definition:

A Systematic Approach for Evaluating Existing Remediation Systems With the Goal of Improving Their Effectiveness and Reducing Overall Site Cleanup Costs

When is an RPO Evaluation Necessary?

- Remedial Systems That Are Falling Short of Cleanup Goals or Have High O&M Costs
- Prior to 5-year Record of Decision (ROD) Reviews
- Prior to RCRA Permit Reapplications
- Operating Properly and Successfully (OPS) Demonstrations

Define Optimization Opportunities

- Source Reduction Optimization
- Define Natural Attenuation Potential
- Plume Containment Optimization, or
- Plume Remediation Optimization
- Long-Term Monitoring Optimization

Potential Cost Savings - Examples

- Larger Systems = Larger Savings
- Monitoring of VOCs at 10 wells vs. 15 wells for 20 years = $40,000
- A 10-HP reduction in pump size over 30 years = $170,000
- Monitored natural attenuation in lieu of a 100 gpm pump and treat system for final 10 years of remediation = $500,000 - $1M

Integration of Natural Attenuation

- Remediation of Choice
- Balance of Time, Risk, and Money
- Account for Contribution of Natural Attenuation within Engineered Remedial Systems
- Changes in Groundwater Chemistry and Natural Attenuation Potential Due to Remedial Systems
- Attenuation of Downgradient Groundwater Contaminant Plumes

Future Direction - Enhanced Natural Bioremediation Of Solvents Via Vegetable Oil Injection

Presented by

Todd H. Wiedemeier

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PARSONS ENGINEERING SCIENCE, INC.

Findings of Natural Attenuation Evaluations - Solvents

- **Intrinsic Bioremediation Occurring at Approximately 88% of the Sites Studied (Biased, Probably 40%)**
- **Reductive Dechlorination Occurring at 100% of Sites Impacted with Fuels**
- **Surface Water Impacted at Many Sites**
- **6 of 13 Plumes Expected to Grow**

Engineered Bioremediation of Chlorinated Solvents

- **Many Types of Organic Substrate Have Been Added to Groundwater to Stimulate Biodegradation of Solvents Including:**
  - **Propionate**
  - **Lactate**
  - **Butyrate**
  - **Molasses**
  - **Hydrogen Releasing Compound®**
  - **Hydrogen ("Hindenberg Experiment")**

Engineered Bioremediation of Chlorinated Solvents

- **All of These Materials are Added to Stimulate the Production of Hydrogen for Reductive Dechlorination**

- **All are Soluble to Some Extent in Water and Many are Miscible**

- **This Means Continuous Injection or at a Minimum, Multiple Injections (With the Exception of HRC®)**

AFCEE VegOil Initiative

- Many Sites Contaminated with Chlorinated Solvents are Electron-Donor Limited
- In 1999, AFCEE Began an Initiative to Enhance Natural Processes of Biodegradation
- Called the "VegOil" Process

VegOil for Engineered Bioremediation of Chlorinated Solvents

- Involves Injection of Food-Grade Vegetable Oil Which is Only Slightly Soluble in Groundwater (~1000 mg/L)
- Costs $0.20 to $0.50/pound
- Should Allow a One-Time Injection Scenario – Big Benefit/Cost Savings
- Soybean Oil is Being Tested at Two Sites; One in Florida and One in Utah

VegOil Concept

- Carbon is Known to Stimulate Biodegradation of Chlorinated Solvents
- Limited by Cost of Carbon and Injection O&M
- Interdisciplinary Team Formed to Test VegOil
  - AFCEE
  - Parsons ES- Environmental Engineering
  - Don Banks - Vegetable Oil Chemistry
  - Dave McWhorter - Multi-Phase Flow

VegOil State of the Art

- 1st In Situ Injection at CCAS
- 2nd In Situ Injection at DDHU
- 2000 Planned injections
  - CCAS Phase 2
  - DDHU, 2 sites
  - Travis AFB
  - Others . . . Hill AFB (Montgomery Watson)
- Other Workers
  - USDA/CSU
  - Monsanto
  - Stanford
  - UNC

Cape Canaveral Air Station

- Industrial Area
- Large Plume of TCE
- Sand Aquifer – Depth to Groundwater 5 feet
- Injected 120 gallons of Soybean Oil and Recovered 40 gallons

Chronology of Vegetable Oil Injection Demonstration

- Demonstration will be conducted in two phases
  - Phase 1 – pilot testing and reporting (6/99-3/00)
  - Phase 2 – larger-scale system installation (1/00-6/01)

Cape Canaveral Air Station – Phase 1

- Background contaminant and geochemical sampling conducted in June 1999
- 110 gallons of vegetable oil injected on June 15 and June 16, 1999
- Pumped back 63 gallons of vegetable oil from June 16 through July 7, 1999
- 47 gallons of vegetable oil remain in the aquifer

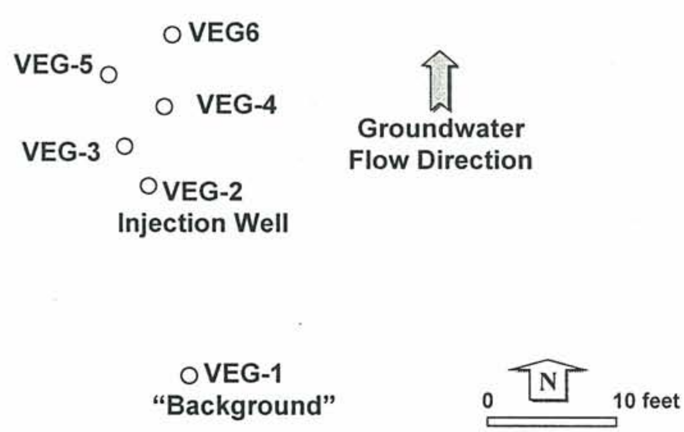
Groundwater Samples Analyzed for:

- Contaminants/ Daughter Products
- Dissolved Oxygen
- Nitrate
- Fe(II)
- Sulfate
- Methane
- Oxidation/Reduction Potential (ORP)
- Carbon Dioxide
- Alkalinity
- pH
- Temperature
- Total Organic Carbon
- Ethene/Ethane
- Chloride
- Arsenic (2 rounds)

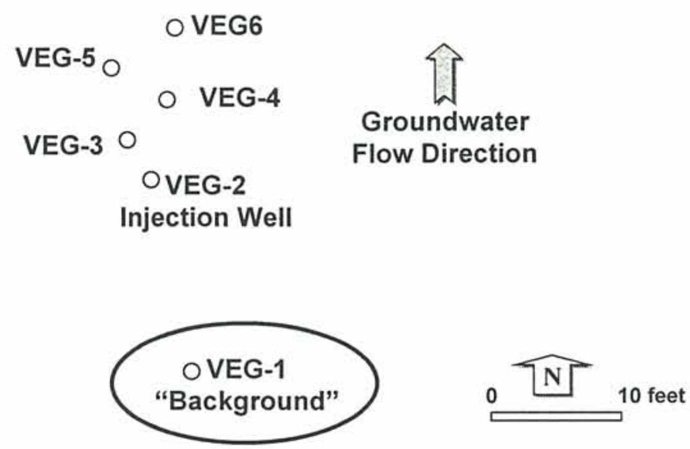
Cape Canaveral Air Station – Phase 1

- Subsequent sampling rounds conducted monthly from July through December 1999
- Data for first five rounds have been analyzed, some round six data is in
- The report for Phase 1 of the demonstration will present the results for all sampling rounds

Site Map

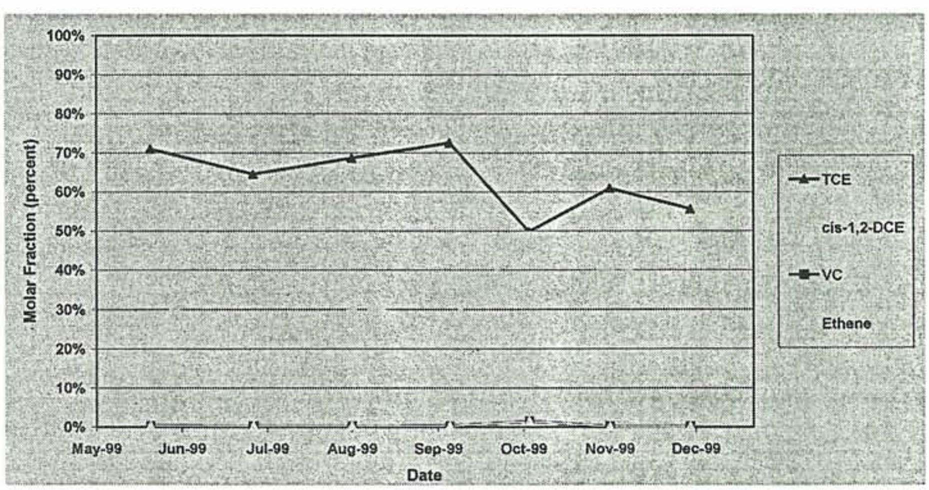


Site Map



vegoil.ppt 1/2000 nap

Molar Fraction of Chlorinated Ethenes at Well HGRK-VEG1



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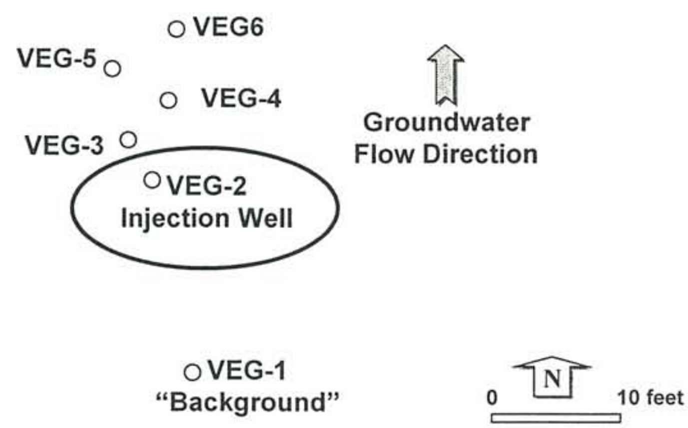

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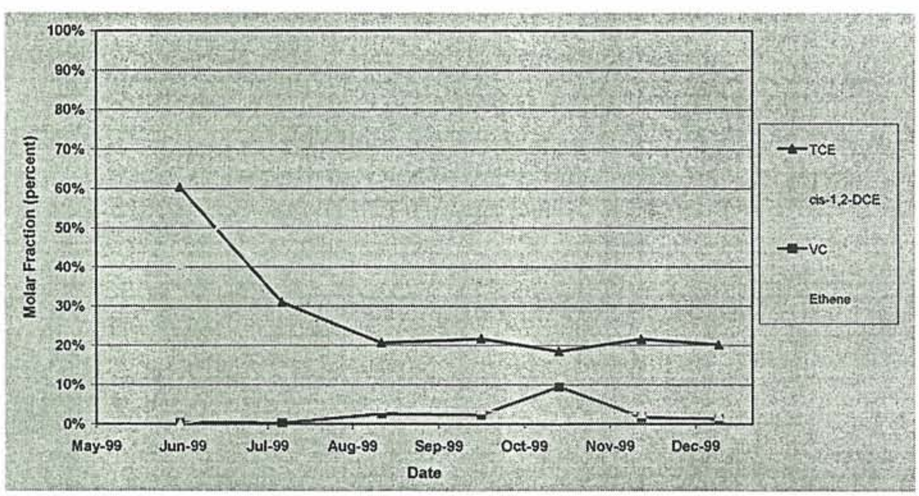
Molar Fraction of Chlorinated Ethenes at Well HGRK-VEG2



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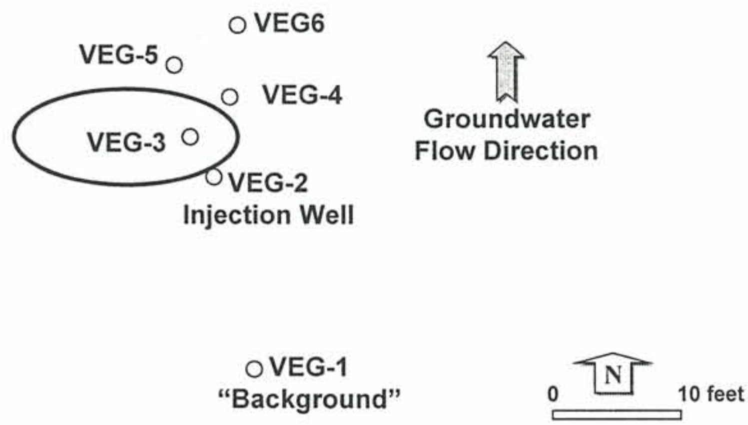

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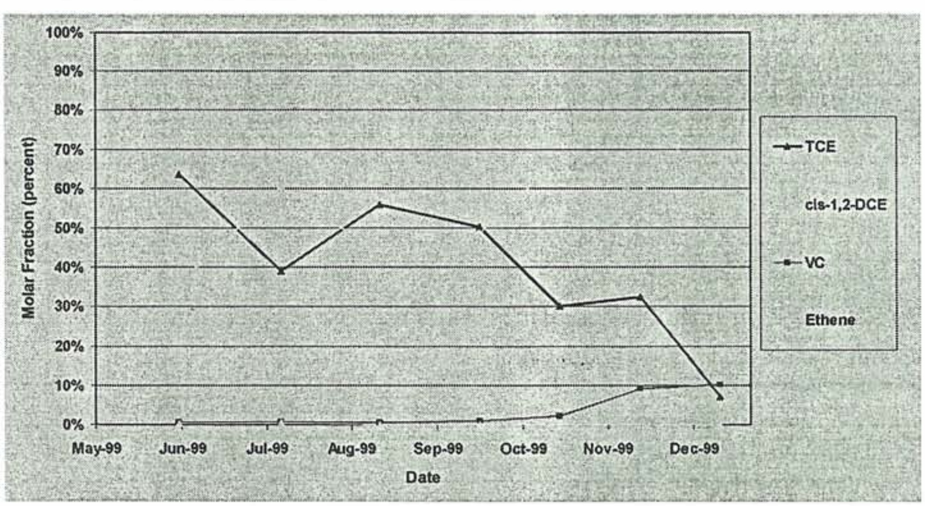
Molar Fraction of Chlorinated Ethenes at Well HGRK-VEG3



vegoil.ppt 1/2000 nap

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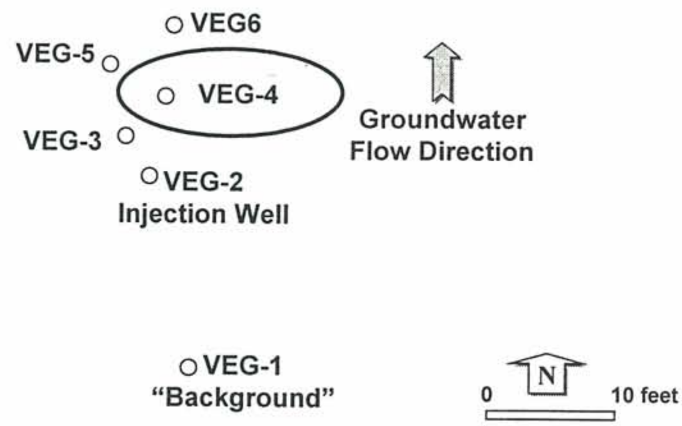
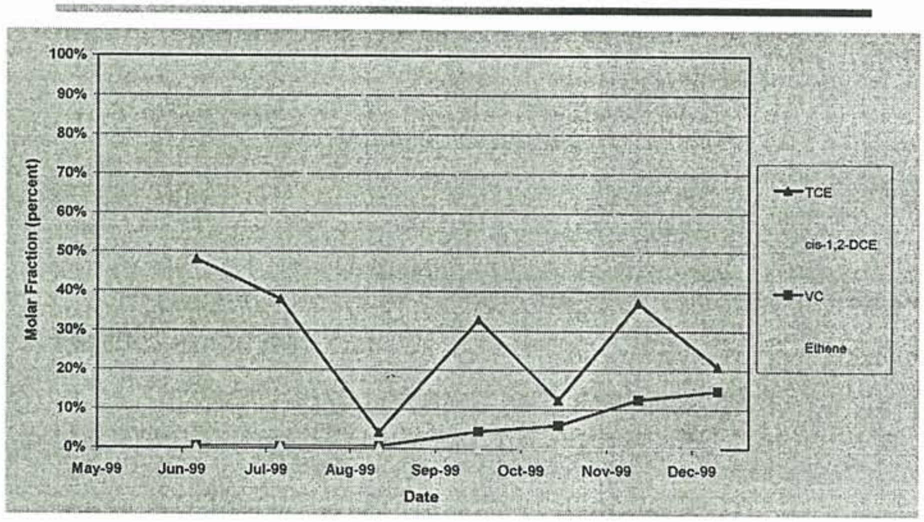
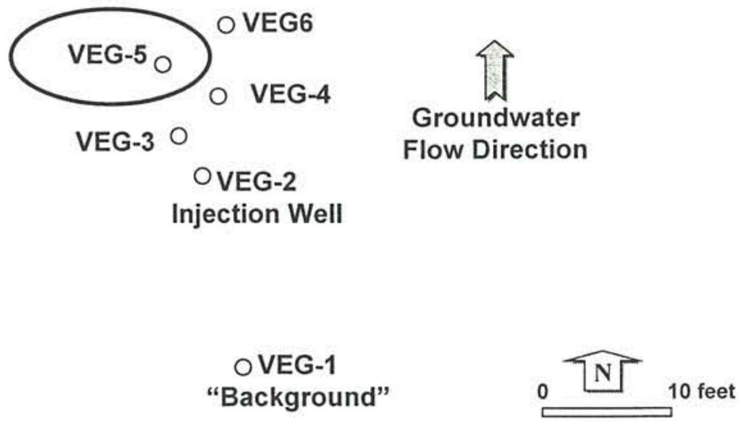


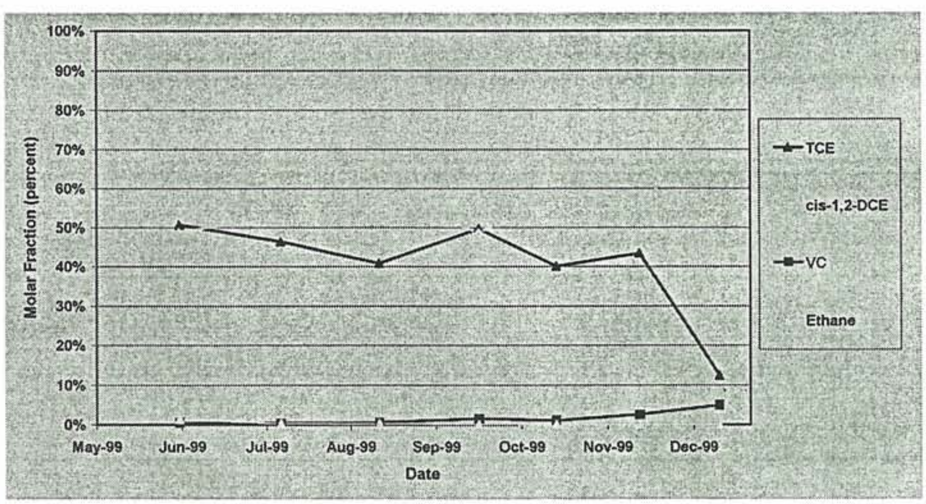
Molar Fraction of Chlorinated Ethenes at Well HGRK-VEG4



Site Map



Molar Fraction of Chlorinated Ethenes at Well HGRK-VEG5



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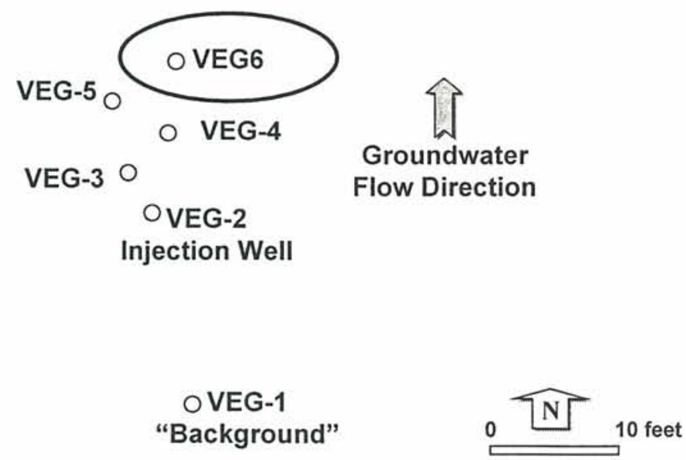
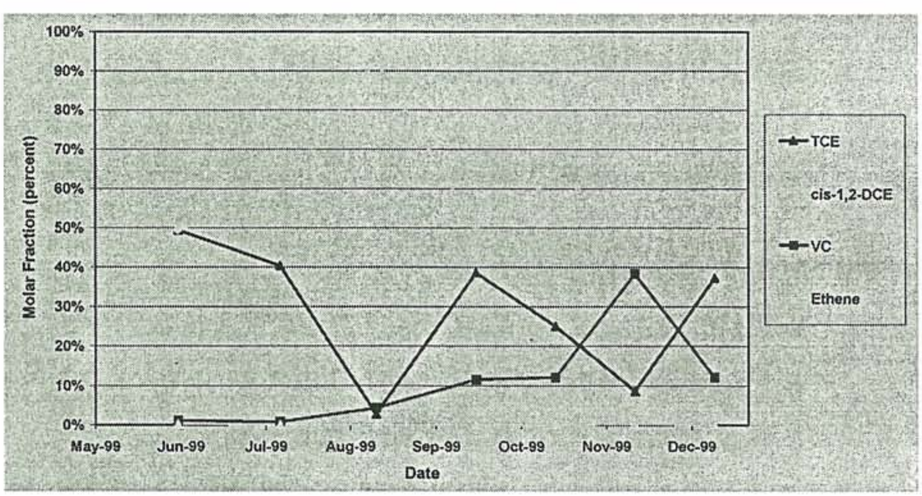


Molar Fraction of Chlorinated Ethenes at Well HGRK-VEG6



Conclusions – Phase 1

- Preliminary Results Look Promising
- TCE Concentrations are Down
- cis-1,2-DCE Concentrations are Up
- More Work is Needed

Cape VegOil - Remaining Questions

- Complete VC dechlorination?
  - Will it happen?
  - Does it need to?
- Application Optimization
  - Ri of Injection Points
  - Pure Oil vs. Emulsion
  - Refine Injection Techniques

Cape Canaveral Air Station – Phase 2

- Phase 2 will involve installation of a "cutoff wall" type remediation system
- System will be 200 feet wide by 30 feet deep
- Work plan being prepared now, draft by 3/00
- Field mobilization/system installation Summer 2000

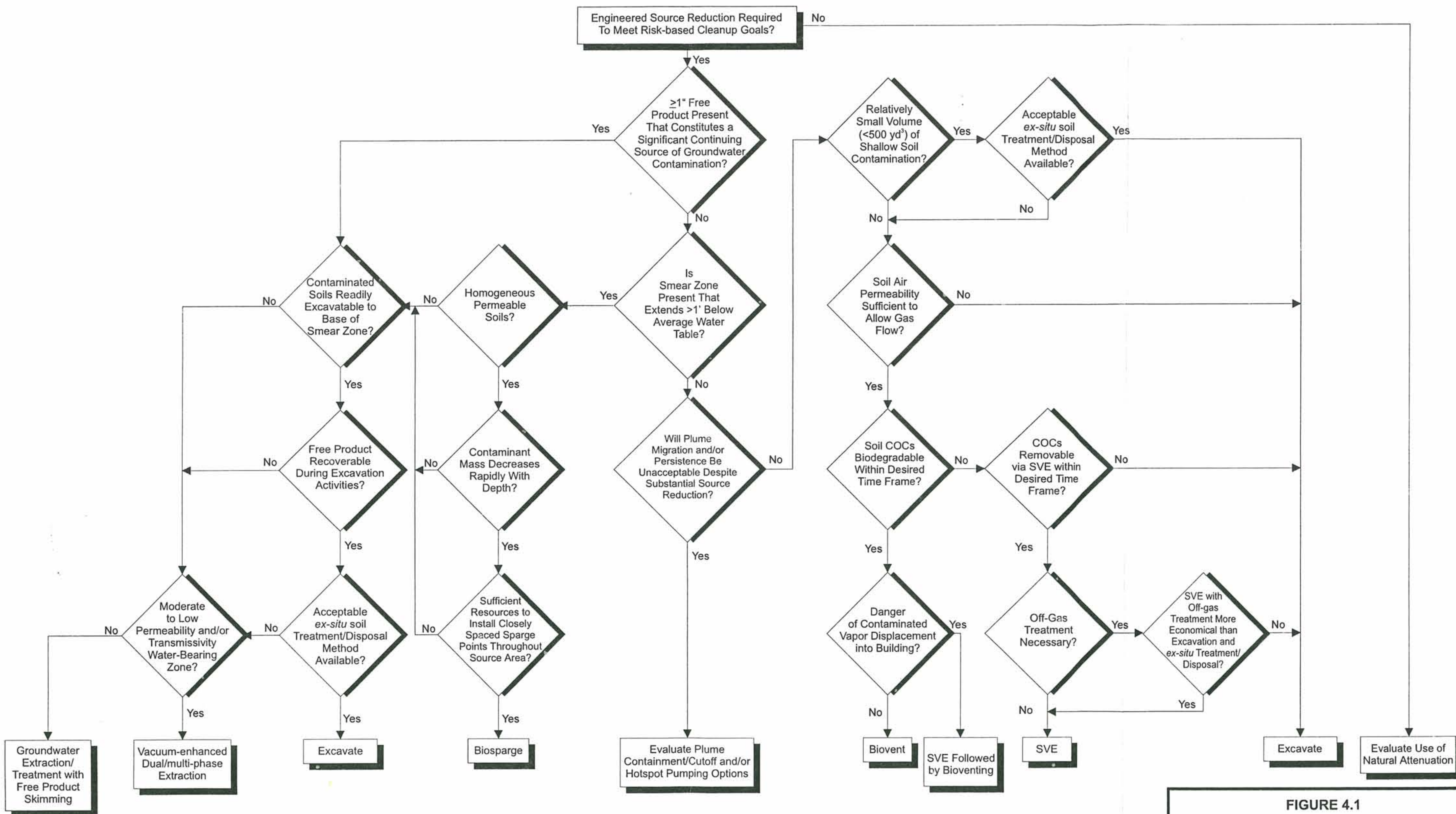


FIGURE 4.1

METHODOLOGY FOR SELECTING AN ENGINEERED SOURCE REDUCTION TECHNIQUE

Source-Reduction Effectiveness Study

PARSONS

PARSONS ENGINEERING SCIENCE, INC.

Denver, Colorado

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